

Synthesis of Novel Heterotetrametallic (d⁶-d¹⁰-d⁸) Polyalkynyl Complexes Starting from Heterobimetallic Chloride-Bridged (d⁶-d⁸) Compounds

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Dedicated to Prof. R. Usón on the occasion of his 75th birthday

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The reaction between the half-sandwich cyclopentadienyl complexes $[M(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2(\text{PEt}_3)]$ ($M = \text{Rh, Ir}$) and $[cis\text{-}M'(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ ($M' = \text{Pt, Pd}$; thf = tetrahydrofuran) affords the corresponding chloride-bridged heterobinuclear Rh, Ir/Pt, Pd complexes $[(\text{PEt}_3)(\eta^5\text{-C}_5\text{Me}_5)M(\mu\text{-Cl})_2M'(\text{C}_6\text{F}_5)_2]$ (**1–4**). In contrast, similar reactions with the chloro-bridged binuclear compounds $[(M(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}(\mu\text{-Cl}))_2]$ ($M = \text{Rh, Ir}$) lead instead to the unexpected mixed salt complexes $\{\text{Cp}^*M(\mu\text{-Cl})_3\text{MCp}^*\}_2\{[(\text{C}_6\text{F}_5)_2M'(\mu\text{-Cl})_2]\}$ ($M = \text{Rh, Ir}$; $M' = \text{Pt, Pd}$) (**5–8**) as a result of chloride transfer. The structures of $[(\text{PEt}_3)(\eta^5\text{-}$

$\text{C}_5\text{Me}_5)\text{Rh}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**1**) and $\{\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RhCp}^*\}_2\{[(\text{C}_6\text{F}_5)_2\text{Pd}(\mu\text{-Cl})_2]\}$ (**6**) have been determined by X-ray diffraction analyses. The reactivity of the new chloride-bridged heterobinuclear compounds **1–4** towards the alkynylating agents $[M''(\text{C}\equiv\text{CR})]_n$ ($M'' = \text{Cu, Ag}$) has also been investigated: a new type of tetranuclear product, $[(\text{PEt}_3)\text{Cp}^*M(\mu\text{-}1\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2M''_2(\mu\text{-}4\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ ($M = \text{Rh, Ir}$; $M'' = \text{Cu, Ag}$) (**9–12**), was obtained, and fully characterized in the case of complex $[(\text{PEt}_3)\text{Cp}^*\text{Rh}(\mu\text{-}1\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Cu}_2(\mu\text{-}4\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**9**).

Introduction

The chemistry of bimetallic complexes has aroused much interest and has led to great development in the field of organometallic chemistry.^[1] In this area, there have been many reports detailing the preparation and chemistry of symmetrical or asymmetrical dichloro-bridged homobinuclear complexes,^{[2][3]} mainly because they play a prominent role as starting materials in organometallic chemistry and because of their relevance in catalysis. In marked contrast, the heterobinuclear analogues $L_m(\mu\text{-Cl})_2M'L_n$ ^[3a–3e] are very scarce and their chemistry remains essentially undocumented, although efforts to develop this chemistry have recently been reported.^[3f–3p]

This paucity of heterobinuclear compounds containing chloride bridging ligands, as well as the potentially rich chemistry that may be expected in these systems, prompted us to prepare binuclear compounds containing Rh^{III} or Ir^{III} fragments together with $[cis\text{-}M'(\text{C}_6\text{F}_5)_2]$ ($M' = \text{Pt, Pd}$) units. We were interested in using these systems as precursors for alkynyl-bridged heteropolynuclear complexes.^[4] In the course of our ongoing research on alkynyl complexes, we have recently succeeded in synthesizing the first homo-bridged bis(μ -alkynyl) $[(\text{PEt}_3)\text{Cp}^*M(\mu\text{-C}\equiv\text{CR})_2M'(\text{C}_6\text{F}_5)_2]$

and hetero-bridged μ -alkynyl, μ -halide $[(\text{PEt}_3)\text{Cp}^*M(\mu\text{-C}\equiv\text{CR})(\mu\text{-X})M'(\text{C}_6\text{F}_5)_2]$ heterobinuclear Rh, Ir^{III}/Pt, Pd^{II} complexes,^[4g] simply by treating mono $[\text{MCp}^*(\text{C}\equiv\text{CR})\text{X}(\text{PEt}_3)]$ or bis(alkynyl) $[\text{MCp}^*(\text{C}\equiv\text{CR})_2(\text{PEt}_3)]$ compounds with $[cis\text{-}M'(\text{C}_6\text{F}_5)_2(\text{thf})_2]$. As a continuation of our work in this field, and in order to complete this series with respect to the bridging system, we report herein the synthesis of the dichloro-bridged heterobinuclear complexes $[(\text{PEt}_3)\text{Cp}^*M(\mu\text{-Cl})_2M'(\text{C}_6\text{F}_5)_2]$ ($M = \text{Rh, Ir}$; $M' = \text{Pt}$: **1, Pd**: **2**; $M = \text{Ir, Pd}$; $M' = \text{Pt}$: **3, Pd**: **4**) and the crystal structure of **1**. Furthermore, in order to explore the potential utility of these new compounds, we have attempted the preparation of alkynyl-bridged complexes by treating them with ethynylating agents such as $[\text{CuC}\equiv\text{CR}]_x$ and $[\text{AgC}\equiv\text{CR}]_x$. These reactions led to the synthesis of a new type of heteropolynuclear alkynyl-bridged complexes $[(\text{PEt}_3)\text{Cp}^*M(\mu\text{-}1\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2M''_2(\mu\text{-}4\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ ($M = \text{Rh, Ir}$; $M'' = \text{Cu, Ag}$) (**9–12**), in which two widely divergent bis(alkynyl) metal fragments (d⁶ and d⁸) are connected through d¹⁰ (Cu or Ag) metal ions. We also describe similar reactions between $[\{\text{MCp}^*\text{Cl}(\mu\text{-Cl})\}_2]$ ($M = \text{Rh, Ir}$) and $[cis\text{-}M'(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ ($M' = \text{Pt, Pd}$) that involve chloride-transfer to yield the mixed salt complexes $\{\text{Cp}^*M(\mu\text{-Cl})_3\text{MCp}^*\}_2\{[(\text{C}_6\text{F}_5)_2M'(\mu\text{-Cl})_2]\}$ ($M = \text{Rh, Ir}$; $M' = \text{Pt, Pd}$) (**5–8**), and we present the crystal structure of $\{\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RhCp}^*\}_2\{[(\text{C}_6\text{F}_5)_2\text{Pd}(\mu\text{-Cl})_2]\}$ (**6**).

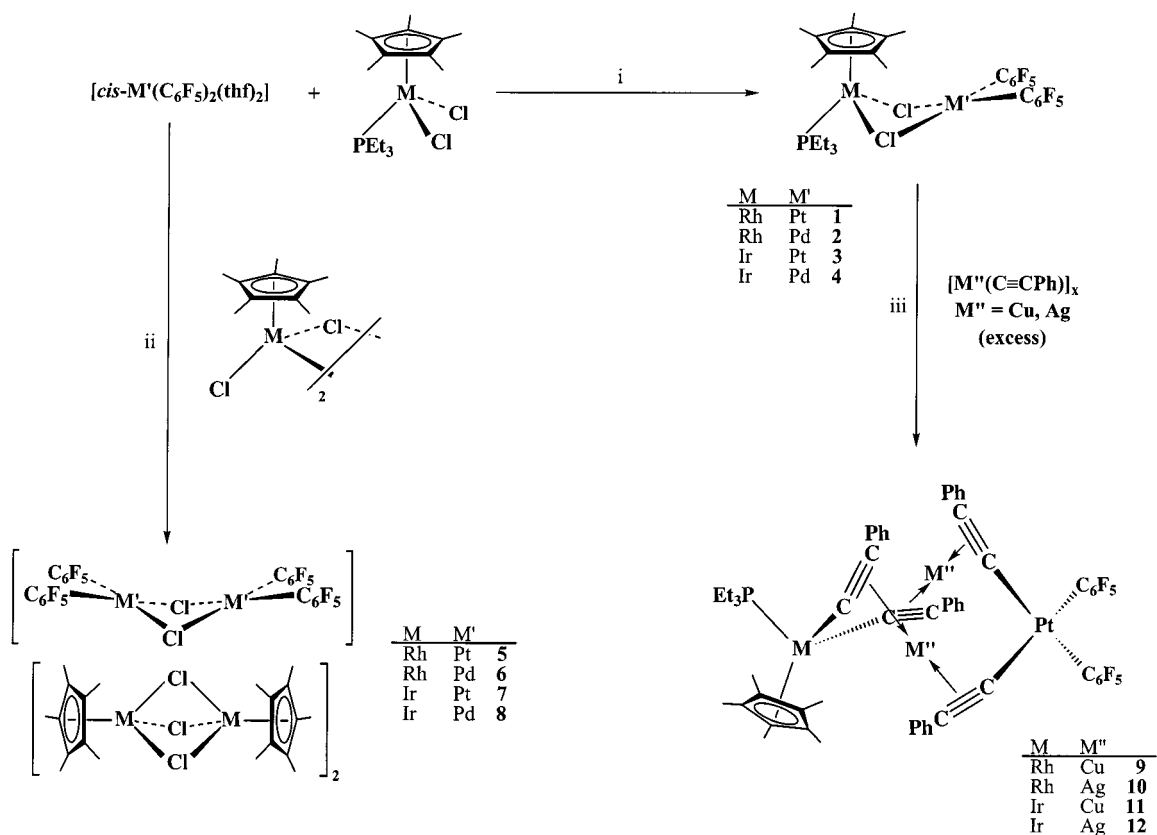
Results and Discussion

Synthesis of Hetero- and Homobimetallic Chloride-Bridged Complexes

The preparative results are summarized in Scheme 1. The reaction of compounds $[cis\text{-}M'(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ ($M' = \text{Pt, Pd}$)

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Scheme 1

with metallo species bearing potentially bridging groups in *cis* or even *trans* positions has proved to be an excellent preparative method for the synthesis of bi- and polymetallic complexes.^[4a,4g,5] Therefore, we considered it appropriate to use this strategy for the synthesis of the desired doubly chloride-bridged heterobinuclear complexes **1–4**. Treatment of a red solution of $[\text{MCp}^*\text{Cl}_2(\text{PEt}_3)]$ ($\text{M} = \text{Rh}, \text{Ir}$) in acetone with 1 equivalent of the solvated platinum or palladium complex $[\text{cis-M}'(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ immediately gave an orange solution, from which the corresponding complexes **1–4** could be isolated as orange solids in high yields (i, Scheme 1). It should be mentioned that several neutral $[(\text{ppy})_2\text{M}(\mu\text{-Cl})_2\text{M}'(\text{PR}_3)\text{Cl}]$ ($\text{M} = \text{Rh}, \text{Ir}; \text{M}' = \text{Pt}, \text{Pd}$; $\text{ppy} = 2\text{-phenylpyridine anion}$; $\text{R} = \text{Bu}, \text{Et}$) or cationic $[(\text{chel})\text{M}(\mu\text{-Cl})_2\text{M}'(\text{PEt}_3)_2](\text{BF}_4)$ ($\text{M} = \text{Rh}, \text{Ir}; \text{M}' = \text{Pt}, \text{Pd}$; $\text{chel} = \text{anion of } 2\text{-phenylpyridine, benzo[4]quinoline, C}_6\text{H}_5\text{CHRNMe}_2, \text{ or } \eta^3\text{-allyl}$) heterobinuclear ($d^6\text{-}d^8$) chloride-bridged complexes have been very recently prepared by metathesis reactions from the respective chloro-bridged homodimeric compounds.^[31,30] In addition, related dicationic $[(\text{PMe}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})_2\text{PtL}_2]^{2+}(\text{OTf})_2^-$ ($\text{M} = \text{Rh}, \text{Ir}; \text{L}_2 = \text{dppp}, 2 \text{ PPh}_3$) complexes have been prepared by a similar route starting from the bis(triflate) species $[\text{MCp}^*(\text{PMe}_3)(\text{OTf})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) and the corresponding dichloroplatinum derivatives.^[3g]

The heterobinuclear platinum complexes **1** and **3** remain stable indefinitely, both in the solid state and in solution, but the mixed palladium compounds are only stable in the solid state. In solution, **2** and **4** slowly decompose with the

deposition of metallic palladium. The complexes have been characterized by analytical and spectroscopic techniques. In addition, the structure of complex **1** has been established by an X-ray diffraction study. The IR spectra show two absorptions in the $785\text{--}812 \text{ cm}^{-1}$ region attributable to the x -sensitive mode of the C_6F_5 groups ($A', A''; C_s$), thus indicating the presence of a *cis*- $\text{M}(\text{C}_6\text{F}_5)_2$ moiety.^[6] Furthermore, all the complexes show bands ($247\text{--}277 \text{ cm}^{-1}$) associated with the $\nu(\text{M}\text{--Cl})$ stretching vibrations ($2A' + 2A''; C_s$) of the bridges.

The NMR spectroscopic data are consistent with the solid-state structure of complex **1**. This complex crystallizes with a bent RhCl_2Pt central core, and the conformer found (see Figure 1) is that in which the $\text{Pt}(\text{C}_6\text{F}_5)_2$ unit lies *endo* to the Cp^* ligand. The room and low-temperature NMR spectroscopic data (^1H , $^{31}\text{P}\{^1\text{H}\}$, ^{19}F , and $^{13}\text{C}\{^1\text{H}\}$) reveal no evidence of possible conformers (see Experimental Section for details), although a possible rapid interconversion of conformers (fast inversion of the central RhCl_2Pt core) cannot be excluded. Only the ^{19}F NMR spectra are temperature dependent. Thus, in accordance with the structure depicted in Scheme 1 (see also Figure 1), the room temperature ^{19}F NMR spectra in $[\text{D}_6]\text{acetone}$ show only one type of C_6F_5 ligand, confirming the equivalence of the two C_6F_5 moieties. However, they exhibit the typical $\text{AA}'\text{MXX}'$ pattern of three signals of relative intensity 2:1:2, evidencing that the two halves of each C_6F_5 ring appear equivalent at room temperature, and indicating that these complexes are not rigid in solution. As expected, on lowering the temper-

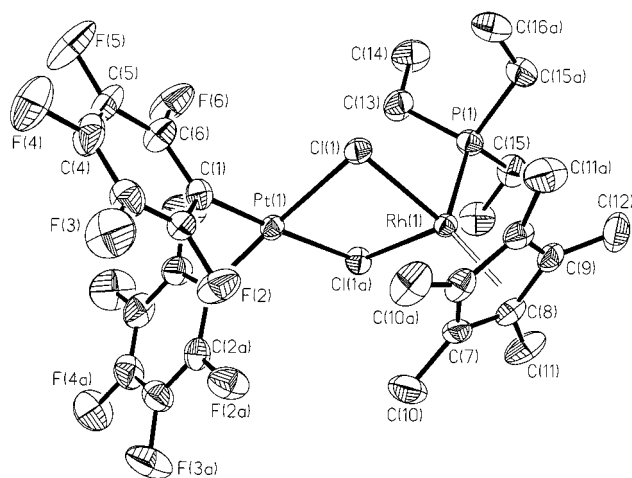


Figure 1. Molecular structure of $[(\text{PEt}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**1**) showing the atom labelling scheme (ellipsoids are drawn at a 50% probability level; hydrogen atoms have been omitted for clarity)

ature (to -50°C), five distinct fluorine resonances become clearly resolved for all the complexes. We note that a possible fast inversion of the central $\text{MCl}_2\text{M}'$ core, which cannot be excluded, would not exchange the two halves of each C_6F_5 moiety. Therefore, the most likely dynamic process that would account for the exchange of the halves of the C_6F_5 rings is their free rotation about the $\text{Pt}-\text{C}(\text{C}_6\text{F}_5)$ bonds. From the coalescence temperature T_c (258 K) and the difference in chemical shift $\Delta\nu$ of the F_o signals, a ΔG^\ddagger value of $51\text{ kJ}\cdot\text{mol}^{-1}$ has been calculated for **4**.^[7] For complex **1**, the ^{19}F NMR spectra have also been recorded in CDCl_3 and both the room and low-temperature (-50°C) spectra were found to be almost identical to those obtained in $[\text{D}_6]\text{acetone}$ solution. This fact suggests that dissociative processes, such as the dissociation of an $\text{M}'(\text{C}_6\text{F}_5)_2$ unit or chloride- M' ($\text{M}' = \text{Pt}, \text{Pd}$) bond breaking, which would probably be solvent dependent, are unlikely.

A definitive structural assignment of the heterobimetallic complexes **1–4** has been established by an X-ray diffraction study on complex $[(\text{PEt}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**1**, Figure 1). Suitable dark-orange crystals were obtained by slow diffusion of hexane into a solution of **1** in acetone at low temperature (-30°C). Selected bond lengths and angles are collected in Table 1. The structure confirms that the complex contains an Rh(III) centre in a pseudo-octahedral environment, formed by the η^5 -bonded C_5Me_5 group, which occupies three formal coordination sites, the PEt_3 , and the two bridging chlorides, and a Pt atom that completes its usual square-planar coordination with two $\sigma\text{-C}_6\text{F}_5$ groups. The geometries around both metal centres are unexceptional for fragments of this type and are similar to those previously observed in related homo-bridged μ -bis(alkynyl) and hetero-bridged ($\mu\text{-Cl})(\mu\text{-alkynyl})$ d^6 - d^8 systems.^[4g] The central $\text{Rh}(\mu\text{-Cl})_2\text{Pt}$ core shows a marked deviation from planarity, with a dihedral angle between the ClRhCl plane and the platinum coordination plane of 31.5° . This structural feature contrasts with the planar cores previously found in the corresponding doubly

chloride-bridged symmetrical bimetallic species $(\text{NBu}_4)_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ ^[8] and $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}(\mu\text{-Cl})\}_2]$.^[9] A recent theoretical study seems to confirm the observation that asymmetric chloro-bridged complexes tend to have a bent structural arrangement.^[3p] Thus, the cationic mixed derivative $[(\text{bzq})_2\text{Rh}(\mu\text{-Cl})_2\text{Pt}(\text{PBu}_3)_2]^+$ is also considerably bent (29.4°)^[3o] and similar nonplanar structures, albeit less severely distorted, have also been found in $[(\text{PMe}_3)\text{Cp}^*\text{Ir}(\mu\text{-Cl})_2\text{Pt}(\text{dppp})]^{2+}$ (ca. 11°)^[3g] and $[(\text{ppy})_2\text{Rh}(\mu\text{-Cl})_2\text{PtCl}(\text{PBu}_3)]$ (13.2°).^[31] However, other theoretical and structural analyses of square-planar d^8 metal complexes of the type $[\text{L}_2\text{M}(\mu\text{-Cl})_2\text{ML}_2]$ seem to suggest that attractive metal–metal interactions are one of the main factors responsible for the observed bending.^[10] In complex **1**, the Pt–Rh distance of $3.407(1)\text{ \AA}$ suggests that the observed puckering does not lead to any significant metal–metal bonding interaction. However, this distance is markedly shorter than those observed in the respective homobimetallic species $[\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Cl})\}_2]^{2-}$ [$3.528(1)\text{ \AA}$]^[8] and $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}(\mu\text{-Cl})\}_2]$ [$3.719(1)\text{ \AA}$]^[9] and in the mixed $\text{Rh}^{\text{III}}-\text{Pt}^{\text{II}}$ *ortho*-metallated derivatives $[(\text{ppy})_2\text{Rh}(\mu\text{-Cl})_2\text{PtCl}(\text{PBu}_3)]$ (3.61 \AA)^[31] and $[(\text{bzq})_2\text{Rh}(\mu\text{-Cl})_2\text{Pt}(\text{PBu}_3)_2]^+$ (3.63 \AA).^[3o] Clearly, the value mentioned above is more akin to that found in the chloride/alkynide hetero-bridged compound $[(\text{PEt}_3)\text{Cp}^*\text{Rh}(\mu\text{-Cl})(\mu\text{-C}\equiv\text{CPh})\text{Pt}(\text{C}_6\text{F}_5)_2]$ [$3.371(1)\text{ \AA}$].^[4g]

Table 1. Selected bond lengths [\AA] and angles [deg.] in complex $[(\text{PEt}_3)\text{Cp}^*\text{Rh}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**1**) (Cp^*cent : centroid of the Cp^* group. Symmetry transformations used to generate equivalent atoms (a): $x, -y + 1/2, z$)

| | | | |
|--------------------------------|-----------|------------------------------------|-----------|
| Rh–Cl(1) | 2.409(1) | Rh–P | 2.313(2) |
| Rh– Cp^*cent | 1.799(1) | Pt–C(1) | 1.959(4) |
| Pt–Cl(1) | 2.381(1) | Rh...Pt | 3.407(1) |
| P–Rh–Cl(1) | 89.27(4) | Cl(1)–Rh–Cl(1a) | 84.02(5) |
| P–Rh– Cp^*cent | 133.04(5) | Cl(1)–Rh– Cp^*cent | 123.48(3) |
| Pt–Cl(1)–Rh | 90.65(3) | C(1)–Pt–C(1a) | 90.6(2) |
| C(1)–Pt–Cl(1) | 92.07(12) | Cl(1)–Pt–Cl(1a) | 85.22(5) |

The bridging chloride is slightly asymmetric, with metal–chlorine distances $[\text{Rh}-\text{Cl}(1)\ 2.409(1)\text{ \AA}; \text{Pt}-\text{Cl}(2)\ 2.381(1)\text{ \AA}]$ rather similar to those found in $[(\text{PEt}_3)\text{Cp}^*\text{Rh}(\mu\text{-Cl})(\mu\text{-C}\equiv\text{CPh})\text{Pt}(\text{C}_6\text{F}_5)_2]$ ($\approx 2.43\text{ \AA}$). This structural feature is in marked contrast to the dichloro bridges in the cationic $[(\text{bzq})_2\text{Rh}(\mu\text{-Cl})_2\text{Pt}(\text{PBu}_3)_2]^+$ and neutral $[(\text{ppy})_2\text{Rh}(\mu\text{-Cl})_2\text{PtCl}(\text{PBu}_3)]$ complexes, which are highly asymmetric ($\text{Rh}-\text{Cl} \approx 2.53\text{ \AA}; \text{Pt}-\text{Cl}\ 2.36\text{--}2.40\text{ \AA}$). The $\text{Cl}(1)\text{RhCl}(1a)$ [$84.02(5)^\circ$] and $\text{Cl}(1)\text{PtCl}(1a)$ [$85.22(5)^\circ$] angles are almost identical and are slightly smaller than the angle at the chlorine atom [$90.65(3)^\circ$].

With the aim of obtaining binuclear derivatives of the general formula $[(\text{S})\text{Cp}^*\text{M}(\mu\text{-Cl})_2\text{M}'(\text{C}_6\text{F}_5)_2]$ with one vacant site for bonding, where S could be a solvent molecule such as acetone or thf, we also explored the reactivity of the tetrahydrofuran adducts $[\text{cis-}\text{M}'(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ towards the binuclear derivatives $[\{\text{MCp}^*\text{Cl}(\mu\text{-Cl})\}_2]$ in acetone in a 2:1 molar ratio. However, contrary to our expectations,

these reactions did not afford the desired heterobimetallic complexes; instead, low yields of the mixed ionic 2:1 salts $[\text{Cp}^*\text{M}(\mu\text{-Cl})_3\text{MCp}^*]_2[\{(\text{C}_6\text{F}_5)_2\text{M}'(\mu\text{-Cl})\}_2]$ (**5–8**) (ii, Scheme 1) were obtained. Predictably, better yields were obtained when the reactions were carried out in a 1:1 molar ratio (see Experimental Section). In these reactions, the platinum and palladium fragments “*cis*- $\text{M}'(\text{C}_6\text{F}_5)_2$ ” act as abstractors of chloride ligands giving $[\text{cis}-(\text{C}_6\text{F}_5)_2\text{M}'\text{Cl}]^-$, which dimerizes to $[(\text{C}_6\text{F}_5)_2\text{M}'(\mu\text{-Cl})_2\text{M}'(\text{C}_6\text{F}_5)_2]^{2-}$, thus leaving the binuclear half-sandwich cationic complexes $[\text{Cp}^*\text{M}(\mu\text{-Cl})_3\text{MCp}^*]^+$ with the chloro-bridges. Both cationic $[(\text{Cp}^*\text{M})_2(\mu\text{-Cl})_3]\text{BF}_4$ ($\text{M} = \text{Rh}, \text{Ir}$)^[11a] species have previously been generated in a more rational manner by treating the binuclear neutral derivatives with AgClO_4 or TIBF_4 in CH_2Cl_2 and, in the case of $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RhCp}^*]^+$, also by reaction of $[\{\text{RhCp}^*\text{Cl}(\mu\text{-Cl})\}_2]$ with NaBPh_4 .^[11b] We also note that chloride-transfer reactions between the highly charged fragments $[\text{PtCl}_6]^{2-}$ and $[\text{RhCp}^*(\text{NCMe})_3]^{2+}$,^[12] as well as between the neutral half-sandwich complexes $[\{p\text{-cym}\}\text{RuCl}(\mu\text{-Cl})_2]$ or $[\{\text{MCp}^*\text{Cl}(\mu\text{-Cl})\}_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) and the cationic chloride-bridged palladium(II) substrate,^[30] have been reported previously.

The ionic compounds **5–8**, which were obtained as orange (**5, 6**) or yellow (**7, 8**) solids, are only slightly soluble in organic solvents, the solubility being especially low in the case of the iridium derivatives. These complexes have been characterized by a combination of microanalysis, mass spectrometry [ES(+) and ES(-)], and spectroscopic methods (IR, ^1H and ^{19}F NMR) (see Experimental Section). Mass spectra in the ES(+) mode feature the expected $[\text{M}_2\text{Cp}^*_2\text{Cl}_3]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) ion molecular fragment and in the ES(-) or APCI(-) modes they feature the $[\text{M}'(\text{C}_6\text{F}_5)_2\text{Cl}]^-$ ($\text{M}' = \text{Pt}, \text{Pd}$) ion fragment arising from a fragmentation of the binuclear anion.

The molecular structure of **6** was confirmed by single-crystal X-ray analysis (Figure 2, Table 2). As can be seen, it comprises two $[(\text{Cp}^*\text{Rh})_2(\mu\text{-Cl})_3]^+$ ions and a binuclear dianionic $[(\text{C}_6\text{F}_5)_2\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\text{C}_6\text{F}_5)_2]^{2-}$ ion. The structural features of the cationic fragment are identical to those reported previously^[12,13] hence they are not discussed here.

In contrast, although the crystal structures of the anions $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)_2]^{2-}$ ^[8] and $[(\text{C}_6\text{F}_5)_2\text{Ni}(\mu\text{-Cl})_2\text{Ni}(\text{C}_6\text{F}_5)_2]^{2-}$ ^[14] have been published, the structure of the corresponding dipalladium species remains unknown. Therefore, this study completes the series with its final member, $[(\text{C}_6\text{F}_5)_2\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\text{C}_6\text{F}_5)_2]^{2-}$, providing an opportunity for quantitative structural comparisons. Selected distances and angles are compared in Table 3. It is interesting to note that one of the most remarkable differences can be seen in the $\text{M}'_2\text{Cl}_2$ core. Thus, while the nickel and platinum anions exhibit typical^[3p,10] $\text{M}'_2\text{Cl}_2\text{C}_4$ planar cores (both have a crystallographic centre of inversion), the anion $[(\text{C}_6\text{F}_5)_2\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\text{C}_6\text{F}_5)_2]^{2-}$ found in **6** displays a slightly bent chloro-bridge, with the dihedral angle defined by the corresponding palladium coordination planes being 13° . The resulting $\text{Pd}\cdots\text{Pd}$ distance of $3.464(2)$ Å is, as expected, longer than that found in the nickel derivative $[\text{Ni}\cdots\text{Ni}$ 3.28 Å].^[14] However, assuming covalent radii for Pd and Pt of

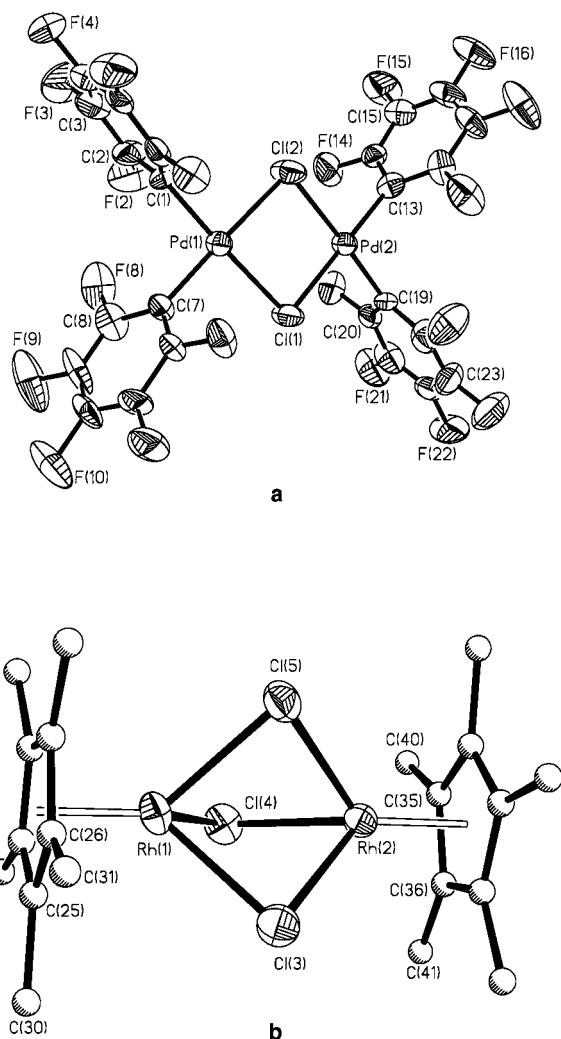


Figure 2. Structure and atom numbering scheme for the anion $[(\text{C}_6\text{F}_5)_2\text{Pd}(\mu\text{-Cl})_2]^{2-}$ (a) and one of the cations $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RhCp}^*]^+$ (b) in complex **6** (ellipsoids are drawn at a 50% probability level; hydrogen atoms have been omitted for clarity)

1.31 and 1.28 Å, respectively,^[15] the $\text{Pd}\cdots\text{Pd}$ distance should be ca. 0.06 Å longer than that found in the dipalladium anion $[\text{Pt}\cdots\text{Pt}$ $3.528(1)$ Å],^[8] thus suggesting that the experimental value found in the dipalladium anion $[3.464(2)$ Å] might be reduced due to the small degree of bending.

The $\text{Pd}-\text{C}$ [$2.001(13)$ – $2.023(12)$ Å] and $\text{Pd}-\text{Cl}$ [$2.404(4)$ – $2.421(4)$ Å] bridging lengths are comparable with those seen in $[(\text{C}_6\text{F}_5)_2\text{Pd}(\mu\text{-Cl})_2\text{Pt}(\text{PEt}_3)_2]$ [$\text{Pd}-\text{C}$ $1.980(7)$, $1.992(7)$ Å; $\text{Pd}-\text{Cl}$ $2.402(2)$, $2.449(2)$ Å], which is the only derivative to be crystallographically characterized that also contains the “ $(\text{C}_6\text{F}_5)_2\text{PdCl}_2$ ” fragment.^[3f]

Synthesis of Tetranuclear $[(\text{PEt}_3)\text{Cp}^*\text{M}(\mu\text{-C}\equiv\text{CPh})_2\text{M}'_2(\mu\text{-C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ Complexes (**9–12**)

We have recently been interested in exploring the reactivity of alkynyl platinate(II) complexes towards suitable electrophilic metal fragments as a useful route to heteropolynuclear complexes containing alkynyl bridging ligands.^[4a,4b,4d–4g,4i–4k] As an alternative route, we decided to examine the potential utility of the new chloride-bridged

Table 2. Selected bond lengths (Å) and angles (deg.) in complex $\{Cp^*Rh(\mu-Cl)_3RhCp^*\}_2\{[(C_6F_5)_2Pd(\mu-Cl)]_2\}$ (**6**) (C*1, C*2, C*3, C*4: centroids of the Cp* groups)

| | | | |
|-------------------|------------|-------------------|------------|
| Pd(1)–C(1) | 2.023(12) | Pd(1)–C(7) | 2.014(12) |
| Pd(1)–Cl(1) | 2.421(4) | Pd(1)–Cl(2) | 2.413(3) |
| Pd(2)–C(13) | 2.008(13) | Pd(2)–C(19) | 2.001(13) |
| Pd(2)–Cl(1) | 2.411(3) | Pd(2)–Cl(2) | 2.404(4) |
| Pd(1)··Pd(2) | 3.464(2) | Rh(1)–C*1 | 1.749(1) |
| Rh(1)–Cl(3) | 2.473(4) | Rh(1)–Cl(4) | 2.469(4) |
| Rh(1)–Cl(5) | 2.473(3) | Rh(2)–C*2 | 1.769(1) |
| Rh(2)–Cl(3) | 2.479(4) | Rh(2)–Cl(4) | 2.472(3) |
| Rh(2)–Cl(5) | 2.476(4) | Rh(1)··Rh(2) | 3.246(2) |
| Rh(3)–C*3 | 1.773(1) | Rh(3)–Cl(6) | 2.467(4) |
| Rh(3)–Cl(7) | 2.452(4) | Rh(3)–Cl(8) | 2.443(4) |
| Rh(4)–C*4 | 1.766(1) | Rh(4)–Cl(6) | 2.480(4) |
| Rh(4)–Cl(7) | 2.472(4) | Rh(4)–Cl(8) | 2.457(4) |
| Rh(3)··Rh(4) | 3.246(2) | | |
| Cl(1)–Pd(1)–Cl(2) | 87.23(12) | Cl(1)–Pd(1)–C(7) | 91.0(4) |
| Cl(2)–Pd(1)–C(1) | 90.0(4) | C(1)–Pd(1)–C(7) | 91.9(5) |
| Cl(1)–Pd(2)–Cl(2) | 87.66(12) | Cl(1)–Pd(2)–C(19) | 91.0(4) |
| Cl(2)–Pd(2)–C(13) | 91.0(4) | C(13)–Pd(2)–C(19) | 90.4(5) |
| Pd(1)–Cl(1)–Pd(2) | 91.60(11) | Pd(1)–Cl(2)–Pd(2) | 91.95(11) |
| Cl(3)–Rh(1)–Cl(4) | 81.49(13) | Cl(3)–Rh(1)–Cl(5) | 82.06(12) |
| Cl(4)–Rh(1)–Cl(5) | 81.49(12) | C*1–Rh(1)–Cl(3) | 130.07(13) |
| C*1–Rh(1)–Cl(4) | 130.90(10) | C*1–Rh(1)–Cl(5) | 131.91(12) |
| Cl(3)–Rh(2)–Cl(4) | 81.31(12) | Cl(3)–Rh(2)–Cl(5) | 81.89(13) |
| Cl(4)–Rh(2)–Cl(5) | 81.39(11) | C*2–Rh(2)–Cl(3) | 130.07(12) |
| C*2–Rh(2)–Cl(4) | 132.05(11) | C*2–Rh(2)–Cl(5) | 130.47(11) |
| Cl(6)–Rh(3)–Cl(7) | 81.7(2) | Cl(6)–Rh(3)–Cl(8) | 81.5(2) |
| Cl(7)–Rh(3)–Cl(8) | 82.2(2) | C*3–Rh(3)–Cl(6) | 130.39(13) |
| C*3–Rh(3)–Cl(7) | 131.17(11) | C*3–Rh(3)–Cl(8) | 131.09(14) |
| Cl(6)–Rh(4)–Cl(7) | 81.0(2) | Cl(6)–Rh(4)–Cl(8) | 81.0(2) |
| Cl(7)–Rh(4)–Cl(8) | 81.5(2) | C*4–Rh(4)–Cl(6) | 131.59(13) |
| C*4–Rh(4)–Cl(7) | 131.71(12) | C*4–Rh(4)–Cl(8) | 130.62(15) |
| Rh(1)–Cl(3)–Rh(2) | 81.94(10) | Rh(1)–Cl(4)–Rh(2) | 82.16(10) |
| Rh(1)–Cl(5)–Rh(2) | 81.99(10) | Rh(3)–Cl(6)–Rh(4) | 81.72(12) |
| Rh(3)–Cl(7)–Rh(4) | 82.18(13) | Rh(3)–Cl(8)–Rh(4) | 82.67(12) |

Table 3. Comparison of selected bond lengths [Å] and angles [deg.] in the anions $[(C_6F_5)_2M'(\mu-Cl)_2M'(C_6F_5)_2]^{2-}$

| Parameter | M' = Ni | M' = Pd | M' = Pt |
|--------------------------|----------|------------------------------|-----------|
| M'–C _{average} | 1.880(3) | 2.012(13) | 1.984(10) |
| M'–Cl _{average} | 2.253(1) | 2.412(4) | 2.391(3) |
| Cl–M'–Cl | 86.71(3) | 87.45(12) _{average} | 84.9(1) |
| M'–Cl–M' | 93.29(3) | 91.78(11) _{average} | 95.1(1) |
| M'····M' | 3.28 | 3.464(2) | 3.528(1) |

heterobinuclear compounds **1–4** as precursors to alkynyl-bridged species by exploring their reactivity towards the well-known ethynylating agents $[M''(C\equiv CR)]_x$ ($M'' = Cu, Ag; R = Ph, tBu$). The reactions of the polymeric acetylides $[Cu(C\equiv CR)]_x$ and $[Ag(C\equiv CR)]_x$ with transition metal halide complexes $[ML_nX_m]$ have been extensively investigated. Simple substitution processes giving the corresponding mononuclear complexes $[ML_n(C\equiv CR)_m]$, as well as the formation of polynuclear species generated by further interaction of the latter with MX species ($X = \text{halide or } C\equiv CR$), have been reported.^[4g,16]

The results of the reactions of **1–4** with $[M''(C\equiv CR)]_x$ ($M'' = Cu, Ag; R = Ph, tBu$) are shown in Scheme 1 (iii). As can be seen, only the treatment of the platinum mixed species $[(PEt_3)Cp^*M(\mu-Cl)Pt(C_6F_5)_2]$ (**1, 3**) with the phenylethynyl substrates (10 equiv. for **9** and 4.5 equiv. for **10–12**)

produces, after standard work-up, moderate (61–75%) or low yields (RhAg₂Pt **10**, 27%) of yellow products that can be formulated as tetrametallic compounds $[(PEt_3)Cp^*M(\mu-1\kappa C^{\alpha}:\eta^2-C\equiv CPh)_2M''_2(\mu-4\kappa C^{\alpha}:\eta^2-C\equiv CPh)_2Pt(C_6F_5)_2]$ ($M = Rh, Ir; M'' = Cu, Ag$) (**9–12**). Unfortunately, starting from the mixed palladium complexes **2** and **4**, considerable decomposition takes place and the analogous reactions with the *tert*-butyl alkynyl substrates $[M''C\equiv C^tBu]_x$ ($M = Cu, Ag$) yield only complicated mixtures of products, which we have not been able to separate. We also note that the reactions of **1** and **3** with a smaller excess of the polymeric alkynides (2 equivalents) produced mixtures of compounds in which the final tetranuclear species and the heterobinuclear $[(PEt_3)Cp^*M(\mu-C\equiv CPh)(\mu-Cl)Pt(C_6F_5)_2]$ were easily detectable by $^{31}P\{^1H\}$ NMR spectroscopy.

The new tetranuclear compounds **9–12** have been fully characterized by analytical and spectroscopic means and the molecular structure of **9** has been unambiguously confirmed by X-ray diffraction analysis. The presence of bridging alkynyl ligands is evident from the IR spectra, which show two $\nu(C\equiv C)$ absorptions in the expected region (1969–2070 cm^{-1}).^[4,16] These bands appear at lower frequencies in the copper derivatives [2009 (s br), 1969 (sh) cm^{-1} **9**; 2006 (s), 1969 (s) cm^{-1} **11**] than in their silver counterparts [2059 (s br) cm^{-1} **10**; 2070 (m), 2036 (m) cm^{-1} **12**] suggesting, in line with previous observations,^[16–18] that the η^2 -alkyne metal interaction is stronger in copper than in silver complexes. Their NMR spectra ($^1H, ^{31}P$) confirm the presence of different groups (Cp*, PEt₃, C≡CPh) and, in particular, the room temperature ^{19}F NMR spectra reveal effective mirror planes that render the two C₆F₅ ligands equivalent. Simple AA'MXX' (2 F_o, F_p, 2 F_m) patterns are seen for all the complexes, presumably because the free rotation of the C₆F₅ rings is relatively fast at room temperature. However, low-temperature spectra could not be obtained due to the low solubilities of the complexes. Furthermore, their relatively low stabilities in solution at room temperature also precluded characterization by $^{13}C\{^1H\}$ NMR spectroscopy. Yellow crystals of $[(PEt_3)Cp^*Rh(\mu-C\equiv CPh)_2Cu_2(\mu-C\equiv CPh)_2Pt(C_6F_5)_2]$ **9** suitable for an X-ray diffraction study were isolated by slow diffusion of hexane into a CH₂Cl₂ solution at low temperature (–30 °C). Figure 3 depicts its molecular structure, while selected bond lengths and angles are summarized in Table 4.

The most remarkable aspect of the structure is that two very different bis(alkynyl) metal fragments “RhCp*(C≡CPh)₂(PEt₃)” and “*cis*-Pt(C₆F₅)₂(C≡CPh)₂” are connected through two copper centres. As for complex **1**, of the two possible conformers of complex **9**, only that in which the platinum unit lies *endo* to the Cp* ring is observed (Figure 3, b). As expected, the Rh centre is tetrahedrally coordinated, being surrounded by the centroid of the Cp* ring, the PEt₃, and two σ -carbon atoms of the alkynyl groups, which act as bridging ligands between the two copper atoms. The Pt atom is located in a slightly distorted square-planar coordination environment made up of four σ -carbon atoms, two from the mutually *cis* C₆F₅ rings and two from the C≡CPh ligands, the latter also being η^2 -bon-

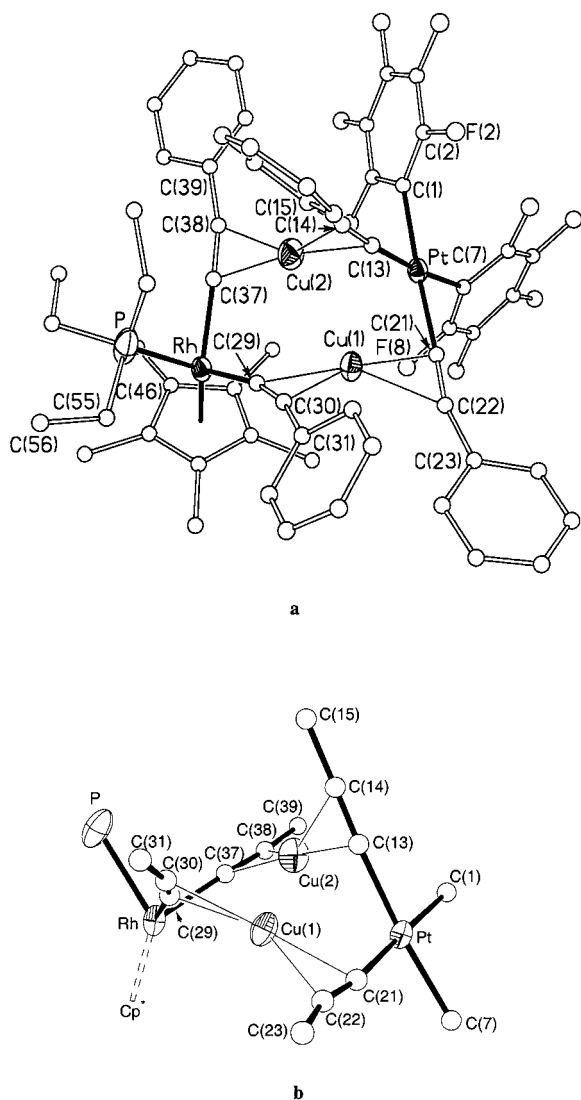


Figure 3. (a) View of the molecular structure of $[(\text{PEt}_3)\text{Cp}^*\text{Rh}(\mu\text{-}1\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Cu}_2(\mu\text{-}4\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**9**) (ellipsoids are drawn at a 50% probability level; hydrogen atoms have been omitted for clarity; (b) schematic view of the central core of **9**)

ded to the copper centres. The structural parameters for this fragment [$\text{Pt}-\text{C}_\alpha$ 2.014(8), 2.001(8) Å; $\text{C}_\alpha-\text{Pt}-\text{C}_\alpha'$ 92.1(3)°] are rather similar to those previously observed for the tetranuclear anion $[\text{Pt}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{C}\equiv\text{CPh})_4]^{2-}$, in which two identical $[\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{C}\equiv\text{CPh})_2]^{2-}$ units are connected via two silver centres through η^2 -alkyne–silver interactions.^[16j]

The most remarkable feature of the rhodium fragment is that the $\text{C}_\alpha-\text{Rh}-\text{C}_\alpha'$ angle (99.3°) is substantially larger compared to related bite angles in doubly alkynyl-bridged complexes $[(\text{PEt}_3)\text{Cp}^*\text{Ir}(\mu\text{-C}\equiv\text{CR})_2\text{M}'(\text{C}_6\text{F}_5)_2]$ [$\text{M}' = \text{Pt}$, $\text{R} = \text{Ph}$ 79.9(8)°; $\text{R} = \text{SiMe}_3$ 76.9(6)°; $\text{M}' = \text{Pd}$, $\text{R} = \text{Ph}$ 81.0(7)°], in which the 3-irida-1,4-diyne fragments $[\text{Ir}](\text{C}\equiv\text{CR})_2$ act as chelating bidentate ligands.^[4g] This structural feature may be tentatively attributed to the bidentate bridging nature of the $[\text{Rh}](\text{C}\equiv\text{CPh})_2$ unit.

All the alkynyl ligands are η^2 -bonded to Cu atoms in such a way that each Cu is stabilized by two alkyne entities (one associated with each metal fragment). The $\text{Cu}-\text{C}_\alpha$

Table 4. Selected bond lengths (Å) and angles (deg.) in complex $[(\text{PEt}_3)\text{Cp}^*\text{Rh}(\mu\text{-}1\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Cu}_2(\mu\text{-}4\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**9**) (Cp^*cent : centroid of the Cp^* group)

| | | | |
|------------------------------------|------------|------------------------------------|------------|
| Pt–C(21) | 2.001(8) | Pt–C(13) | 2.014(8) |
| Pt–C(1) | 2.065(7) | Pt–C(7) | 2.066(7) |
| Pt–Cu(1) | 2.9226(14) | Pt–Cu(2) | 2.9384(13) |
| Rh–C(37) | 2.006(8) | Rh–C(29) | 2.027(8) |
| Rh–P | 2.289(2) | Cu(1)–C(21) | 2.020(7) |
| Cu(1)–C(30) | 2.080(7) | Cu(1)–C(29) | 2.098(7) |
| Cu(1)–C(22) | 2.194(7) | Cu(1)–Cu(2) | 2.841(2) |
| Cu(2)–C(13) | 1.984(8) | Cu(2)–C(37) | 1.989(7) |
| Cu(2)–C(38) | 2.101(8) | Cu(2)–C(14) | 2.230(8) |
| C(13)–C(14) | 1.222(10) | C(21)–C(22) | 1.233(10) |
| C(29)–C(30) | 1.213(10) | C(37)–C(38) | 1.226(10) |
| Rh– Cp^*cent | 1.871 | Rh–Pt | 5.247 |
| Rh–Cu(1) | 3.528 | Rh–Cu(2) | 3.217 |
| C(21)–Pt–C(13) | 92.1(3) | C(1)–Pt–C(7) | 87.8(3) |
| C(13)–Pt–C(1) | 88.2(3) | C(21)–Pt–C(7) | 91.7(3) |
| Cu(1)–Pt–Cu(2) | 57.99(3) | C(37)–Rh–C(29) | 99.3(3) |
| C(37)–Rh–P | 87.0(2) | C(29)–Rh–P | 83.7(2) |
| C(14)–C(13)–Pt | 175.3(7) | C(13)–C(14)–C(15') | 161.7(13) |
| C(13)–C(14)–C(15) | 176(3) | C(22)–C(21)–Pt | 171.4(7) |
| C(21)–C(22)–C(23) | 163.4(8) | C(30)–C(29)–Rh | 167.7(7) |
| C(29)–C(30)–C(31) | 165.2(8) | C(38)–C(37)–Rh | 173.8(7) |
| C(37)–C(38)–C(39) | 165.7(8) | Cp^*cent –Rh–C(29) | 122.81 |
| Cp^*cent –Rh–C(37) | 122.23 | Cp^*cent –Rh–P | 131.03 |
| Cu(1)–Rh–Cu(2) | 49.56 | | |

[1.984(8)–2.098(7) Å] and $\text{Cu}-\text{C}_\beta$ [2.080(7)–2.230(8) Å] distances are, as expected, shorter than the corresponding $\text{Ag}-\text{C}$ distances in $[\text{Pt}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{C}\equiv\text{CPh})_4]^{2-}$,^[16j] but are comparable to those found in related systems such as $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8]_3$ [$\text{Cu}-\text{C}_\alpha = 1.981(8)$ – $2.019(8)$ Å; $\text{Cu}-\text{C}_\beta = 2.141(9)$ – $2.161(9)$ Å],^[19] $[\text{Ir}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8(\text{PPh}_3)_2]$ [$\text{Cu}-\text{C}_\alpha = 1.981(8)$ – $2.019(8)$ Å; $\text{Cu}-\text{C}_\beta = 2.141(9)$ – $2.161(9)$ Å],^[16a,16b] $[\text{Mn}_2\text{Cu}(\mu\text{-C}\equiv\text{C}t\text{Bu})_2(\text{CO})_6(\text{dppe})_2]^+$ [$\text{Cu}-\text{C}_{\text{average}} = 2.081(10)$ Å],^[20] and $[\{\text{Re}(\text{CO})_5-\text{C}\equiv\text{C}-\text{Re}(\text{CO})_5\}_2\text{Cu}]^+$ [$\text{Cu}-\text{C}_{\text{average}} = 2.055(10)$ Å].^[17] The parameters for the acetylenic fragments ($\text{C}-\text{C}$ distances, angles at C_α and C_β) lie within the normal ranges for alkynyl σ,π bonding modes.^[4,16–20]

The $\text{Cu}(1)\cdots\text{Cu}(2)$ distance [2.841(2) Å] is slightly shorter than those found in the cluster $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8]_3$ [3.031(2) Å, 3.301(2) Å]^[19] and is comparable with those observed in the cluster $[\text{Ir}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8(\text{PPh}_3)_2]$ [2.665(6) Å, 2.823(5) Å]^[16a,16b] and in other more common alkynyl polynuclear copper(I) complexes.^[21] Nevertheless, it still slightly exceeds the van der Waals limit (2.80 Å),^[15] excluding any significant bonding interaction. The $\text{Rh}\cdots\text{Cu}$ separations of 3.217 and 3.528 Å are considerably longer than the $\text{Pt}\cdots\text{Cu}$ distances of 2.9226(14) and 2.9384(13) Å, respectively. These latter values are comparable to those seen in $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8]_3$ [2.9187(12)–3.0272(10) Å]^[19] and are considerably shorter than the sum of the van der Waals radii (3.15 Å),^[15] probably suggesting the presence of some weak $\text{Pt}\cdots\text{Cu}$ bonding interactions.^[22]

Experimental Section

General Remarks: All reactions were carried out under nitrogen atmosphere. Solvents (hexane, alkane mixtures) were dried by

standard procedures and distilled under dry N₂ before use; acetone was treated with KMnO₄ and distilled under dry N₂ prior to use. [MCp*Cl₂(PEt₃)],^[48] [MCp*Cl₂]₂ (M = Rh, Ir),^[23] [MC≡CPh]_x (M = Ag,^[24] Cu^[25]), and [cis-M'(C₆F₅)₂(thf)₂] (M' = Pt, Pd)^[26] were prepared by published methods. – ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on a Bruker ARX-300 spectrometer. Chemical shifts are reported in ppm relative to external standards (SiMe₄, CFC₃, and 88% H₃PO₄) and coupling constants are given in Hz. – Infrared spectra were recorded on a Perkin–Elmer 883 spectrometer with samples as Nujol mulls between polyethylene sheets. – C, H, N analyses were carried out with Perkin–Elmer 2400 CHNS/O or Carlo Erba EA1110 CHNS-O microanalyzers. – Mass spectra were obtained on VG Autospec double-focusing (FAB) or HP-5989B (APCI and ES) mass spectrometers. – Conductivities were measured in ca. 5·10^{−4} M acetone solutions using a Philips 950/01 conductimeter.

Synthesis of [(PEt₃)Cp*M(μ-Cl)₂M'(C₆F₅)₂] (M = Rh, M' = Pt 1, M' = Pd 2; M = Ir, M' = Pt 3, M' = Pd 4): A red solution of [RhCp*Cl₂(PEt₃)] (0.10 g, 0.23 mmol) in acetone (10 mL) was treated with [cis-Pt(C₆F₅)₂(thf)₂] (0.15 g, 0.23 mmol), which immediately afforded an orange solution. The mixture was stirred for 5 min and then concentrated to dryness. Treatment of the solid residue with cold EtOH (ca. 5 mL) furnished complex **1** as an orange solid. Complexes **2–4** (also orange solids) were similarly prepared but with omission of the stirring for 5 min in the case of the palladium complexes **2** and **4**. Reagents and quantities used: [cis-Pd(C₆F₅)₂(thf)₂] (0.14 g, 0.23 mmol) and [RhCp*Cl₂(PEt₃)] (0.10 g, 0.23 mmol) for **2**; [cis-Pt(C₆F₅)₂(thf)₂] (0.34 g, 0.51 mmol) and [IrCp*Cl₂(PEt₃)] (0.26 g, 0.51 mmol) for **3**; [cis-Pd(C₆F₅)₂(thf)₂] (0.11 g, 0.19 mmol) and [IrCp*Cl₂(PEt₃)] (0.10 g, 0.19 mmol) for **4**.

1: (0.20 g, 90%). – C₂₈H₃₀Cl₂F₁₀PPtRh (956.42): calcd. C 35.16, H 3.16; found C 34.97, H 2.87. – IR: $\tilde{\nu}$ = 812 (vs), 800 (vs) cm^{−1} (C₆F₅)_x-sens; 277 (m), 255 (m), 246 (m) cm^{−1} (M–Cl). – ¹H NMR (CDCl₃): at 20 °C: δ = 1.15 (m, 9 H, CH₃, PEt₃), 1.74 (d, ⁴J_{P–H} = 2.6, 15 H, Cp*), 2.23 (m, 6 H, CH₂, PEt₃); at –50 °C: δ = 1.07 (m, 9 H, CH₃, PEt₃), 1.75 (d, ⁴J_{P–H} = 2.7, 15 H, Cp*), 2.20 (m, 6 H, CH₂, PEt₃). – ¹³C NMR ([D₆]acetone): at 20 °C: δ = 7.3 (d, ²J_{P–C} = 3.4, CH₃, PEt₃), 9.3 [s, C₅(CH₃)₅], 15.4 (d, ¹J_{P–C} = 27.8, CH₂, PEt₃), 101.9 (dd, ¹J_{Rh–C} = 7.1, ²J_{P–C} = 2.0, C₅Me₅), 135.95 (dm, ¹J_{F–C} = 253, C_m, C₆F₅), 136.5 (dm, ¹J_{F–C} = 241, C_p, C₆F₅), 148.95 (dm, ¹J_{F–C} = 231, C_o, C₆F₅). – ¹⁹F NMR (CDCl₃): at 20 °C: δ = –163.03 (m, 4 F_m), –163.99 (t, 2 F_p), –119.62 (d, ³J_{Pt–F} = 527.7, 4 F_o); at –50 °C: δ = –165.34 (m, 2 F_m), –164.99 (m, 2 F_m), –163.18 (t, 2 F_p), –119.74 (d, ³J_{Pt–F} ≈ 525, 2 F_o), –119.29 (d, ³J_{Pt–F} ≈ 510, 2 F_o). – ³¹P NMR (CDCl₃): at 20 °C: δ = 30.27 (d, ¹J_{Rh–P} = 138.3); at –50 °C: δ = 31.31 (d, ¹J_{Rh–P} = 137.9). – FAB(+) MS: *m/z* (%) = 955 (5) [M⁺ – 1], 789 (10) [M⁺ – C₆F₅], 391 (100) [RhCp*Cl(PEt₃)⁺].

2: (0.16 g, 78%). – C₂₈H₃₀Cl₂F₁₀PPdRh (867.75): calcd. C 38.76, H 3.48; found C 38.43, H 3.41. – IR: $\tilde{\nu}$ = 798 (s), 785 (s) cm^{−1} (C₆F₅)_x-sens; 268 (m, br) (M–Cl). – ¹H NMR ([D₆]acetone): at 20 °C: δ = 1.17 (m, 9 H, CH₃, PEt₃), 1.81 (d, ⁴J_{P–H} = 3, 15 H, Cp*), 2.38 (m, 6 H, CH₂, PEt₃); at –50 °C: δ = 1.07 (m, 9 H, CH₃, PEt₃), 1.81 (d, ⁴J_{P–H} = 2.7, 15 H, Cp*), 2.32 (m, 6 H, CH₂, PEt₃). – ¹³C NMR ([D₆]acetone): at –50 °C: δ = 6.1 (d, ²J_{P–C} = 3.5, CH₃, PEt₃), 8.0 [s, C₅(CH₃)₅], 14.4 (d, ¹J_{P–C} = 27.8, CH₂, PEt₃), 100.7 (dd, ¹J_{Rh–C} = 7.1, ²J_{P–C} = 2.3, C₅Me₅), 134.4 (dm, ¹J_{F–C} = 257, C_m, C₆F₅), 135.75 (dt, ¹J_{F–C} = 241, ²J_{F–C} ≈ 14, C_p, C₆F₅), 146.2 (dm, ¹J_{F–C} = 226, C_o, C₆F₅). – ¹⁹F NMR ([D₆]acetone): at 20 °C: δ = –165.63 (m, 4 F_m), –163.27 (t, 2 F_p), –114.54 (d, 4 F_o); at –50 °C: δ = –164.89 (m, 4 F_m), –162.31 (t, 2 F_p), –114.47 (d, 2 F_o), –114.21 (d, 2 F_o). – ³¹P NMR ([D₆]acetone): at 20 °C:

δ = 29.66 (d, ¹J_{Rh–P} = 139); at –50 °C: δ = 30.75 (d, ¹J_{Rh–P} = 138.8). – FAB(+) MS: *m/z* (%) = 832 (6) [M⁺ – Cl – 1], 700 (21) [M⁺ – C₆F₅], 391 (100) [RhCp*Cl(PEt₃)⁺].

3: (0.45 g, 85%). – C₂₈H₃₀Cl₂F₁₀IrPPt (1045.73): calcd. C 32.16, H 2.89; found C 31.94, H 2.89. – IR: $\tilde{\nu}$ = 812 (vs), 800 (vs) cm^{−1} (C₆F₅)_x-sens; 285 (s), 276 (s), 253 (s) cm^{−1} (M–Cl). – ¹H NMR ([D₆]acetone): at 20 °C: δ = 1.14 (m, 9 H, CH₃, PEt₃), 1.81 (d, ⁴J_{P–H} = 1.6, 15 H, Cp*), 2.44 (m, 6 H, CH₂, PEt₃); at –50 °C: δ = 1.05 (m, 9 H, CH₃, PEt₃), 1.81 (d, ⁴J_{P–H} = 2.7, 15 H, Cp*), 2.37 (m, 6 H, CH₂, PEt₃). – ¹³C NMR ([D₆]acetone): at –50 °C: δ = 5.4 (d, ²J_{P–C} = 3.3, CH₃, PEt₃), 7.4 [s, C₅(CH₃)₅], 13.5 (d, ¹J_{P–C} = 35.1, CH₂, PEt₃), 93.4 (d, ²J_{P–C} = 2.3, C₅Me₅), 134.25 (dm, ¹J_{F–C} = 260, C_m, C₆F₅), 135.1 (dm, ¹J_{F–C} = 240, C_p, C₆F₅), 147.2 (dm, ¹J_{F–C} = 238, C_o, C₆F₅). – ¹⁹F NMR ([D₆]acetone): at 20 °C: δ = –166.74 (m, ⁴J_{Pt–F} = 124.5, 4 F_m), –164.81 (t, 2 F_p), –118.41 (d, ³J_{Pt–F} = 526.2, 4 F_o); at –50 °C: δ = –165.99 (m, 4 F_m), –163.86 (t, 2 F_p), –118.49 (d, ³J_{Pt–F} ≈ 400, 2 F_o), –117.98 (d, ³J_{Pt–F} = 509.9, 2 F_o). – ³¹P NMR ([D₆]acetone): at 20 °C: δ = 4.57 (s); at –50 °C: δ = 5.80 (s). – FAB(+) MS: *m/z* (%) = 1044 (17) [M⁺ – 2], 878 (6) [M⁺ – C₆F₅], 481 (100) [IrCp*Cl(PEt₃)⁺].

4: (0.13 g, 71%) (analyses for a sample recrystallized from CHCl₃/hexane, which retained a 1/2 molecule of CHCl₃ as observed by ¹H NMR in [D₆]acetone). – C₂₈H₃₀Cl₂F₁₀IrPPd·0.5CHCl₃ requires C 33.67, H 3.02; found C 33.99, H 2.74. – IR: $\tilde{\nu}$ = 798 (s), 785 (s) cm^{−1} (C₆F₅)_x-sens; 285, 280 (s), 268 (m), 247 (sh) cm^{−1} (M–Cl). – ¹H NMR ([D₆]acetone): at 20 °C: δ = 1.16 (m, 9 H, CH₃, PEt₃), 1.81 (d, ⁴J_{P–H} = 1.3, 15 H, Cp*), 2.43 (m, 6 H, CH₂, PEt₃); at –50 °C: δ = 1.14 (m, 9 H, CH₃, PEt₃), 1.81 (s, 15 H, Cp*), 2.43 (m, 6 H, CH₂, PEt₃). – ¹³C NMR ([D₆]acetone): at –50 °C: δ = 7.1 (d, ²J_{P–C} = 3.5, CH₃, PEt₃), 9.05 [s, C₅(CH₃)₅], 13.5 (d, ¹J_{P–C} = 35, CH₂, PEt₃), 94.5 (d, ²J_{P–C} = 2.5, C₅Me₅), 135.9 (dm, ¹J_{F–C} = 244, C_m, C₆F₅), 137.3 (dm, ¹J_{F–C} = 241, C_p, C₆F₅), 147.5 (dm, ¹J_{F–C} = 228, C_o, C₆F₅). – ¹⁹F NMR ([D₆]acetone): at 20 °C: δ = –165.50 (m, 4 F_m), –162.95 (t, 2 F_p), –114.87 (d, 4 F_o); at –50 °C: δ = –164.82 (m, 4 F_m), –162.11 (t, 2 F_p), –114.89 (d, 2 F_o), –114.48 (d, 2 F_o). – ³¹P NMR ([D₆]acetone): at 20 °C: δ = 2.13 (s); at –50 °C: δ = 3.07 (s). – FAB(–) MS: *m/z* (%) = 917 (3) [M[−] – Cl – 4], 477 (100) [Pd(C₆F₅)₂Cl[−]].

Synthesis of [Cp*Rh(μ-Cl)₂RhCp*]₂(C₆F₅)₂Pt(μ-Cl)₂Pt(C₆F₅)₂] (5): To a red solution of [RhCp*Cl₂]₂ (0.10 g, 0.162 mmol) in acetone (20 mL) was added [cis-Pt(C₆F₅)₂(thf)₂] (0.11 g, 0.162 mmol) (molar ratio 1:1) and the mixture was stirred for 30 min. Evaporation of the solvent from the orange suspension and treatment of the solid residue with Et₂O (ca. 5 mL) yielded complex **5** (0.13 g, 68%) as an orange solid. – C₆₄H₆₀Cl₈F₂₀Pt₂Rh₄ (2294.60): calcd. C 33.50, H 2.63; found C 33.45, H 2.65. – Λ_m (acetone) = 184 ohm^{−1}·cm²·mol^{−1}. – IR: $\tilde{\nu}$ = 811 (vs), 799 (vs) cm^{−1} (C₆F₅)_x-sens; 289 (m), 261 (m), 255 (s), 250 (s) cm^{−1} (M–Cl). – ¹H NMR ([D₆]acetone): at 20 °C: δ = 1.77 (s, Cp*). – ¹⁹F NMR ([D₆]acetone): at 20 °C: δ = –167.87 (m, 8 F_m), –166.87 (t, 4 F_p), –117.51 (dd, ³J_{Pt–F} = 526.7, 8 F_o). – APCI(+) MS: *m/z* (%) = 581 (16) [Rh₂Cp*₂Cl₃⁺]. – APCI(–) MS: *m/z* (%) = 565 (100) [Pt(C₆F₅)₂Cl[−]].

Complex **5** could also be obtained, albeit in lower yield (0.09 g, 42% based on Rh), by carrying out the reaction starting from [RhCp*Cl₂]₂ (0.11 g, 0.18 mmol) and [cis-Pt(C₆F₅)₂(thf)₂] (0.24 g, 0.36 mmol) (molar ratio 1:2) and following the same procedure as above.

Synthesis of [Cp*Rh(μ-Cl)₂RhCp*]₂(C₆F₅)₂Pd(μ-Cl)₂Pd(C₆F₅)₂] (6): [cis-Pd(C₆F₅)₂(thf)₂] (0.10 g, 0.16 mmol) was added to a red solution of [RhCp*Cl₂]₂ (0.10 g, 0.16 mmol) in CH₂Cl₂ (20 mL)

(molar ratio 1:1) and the mixture was stirred for 30 min. The resulting solution was then concentrated to a small volume (ca. 5 mL), whereupon **6** (0.14 g, 80%) was precipitated as an orange solid. – $C_{64}H_{60}Cl_8F_{20}Pd_2Rh_4$ (2117.26): calcd. C 36.31, H 2.86; found C 36.16, H 2.58. – Λ_m (acetone) = 167 $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. – IR: $\tilde{\nu}$ = 796 (s), 783 (s) cm^{-1} (C_6F_5) $_{x-\text{sens}}$; 288 (m), 278 (m), 249 (s) cm^{-1} (M–Cl). – $^1\text{H NMR}$ ($[D_6]$ acetone): at 20 °C: δ = 1.77 (s, Cp*). – $^{19}\text{F NMR}$ ($[D_6]$ acetone): at 20 °C: δ = 166.77 (m, 8 F_m), –165.24 (t, 4 F_p), –113.29 (d, 8 F_o). – APCI(+) MS: m/z (%) = 581 (100) [$Rh_2Cp^*_2Cl_3^+$]. – APCI(–) MS: m/z (%) = 477 (16) [$Pd(C_6F_5)_2Cl^-$].

Complex **6** could also be obtained, albeit in lower yield (0.09 g, 58% based on Rh), by carrying out the reaction starting from [$RhCp^*Cl_2$]₂ (0.09 g, 0.15 mmol) and [$cis\text{-Pd}(C_6F_5)_2(\text{thf})_2$] (0.17 g, 0.30 mmol) (molar ratio 1:2) and following the same procedure as described for **5**.

Synthesis of $[Cp^*Ir(\mu\text{-Cl})_2IrCp^*]_2(C_6F_5)_2M'(\mu\text{-Cl})M'(C_6F_5)_2$ ($M' = Pt$ **7, Pd **8**):** Complexes **7** and **8** were prepared in a manner similar to that described for **5**. Reagents and quantities used: [$IrCp^*Cl_2$]₂ (0.10 g, 0.13 mmol) and [$cis\text{-Pt}(C_6F_5)_2(\text{thf})_2$] (0.09 g, 0.13 mmol) for **7**; [$IrCp^*Cl_2$]₂ (0.08 g, 0.10 mmol) and [$cis\text{-Pd}(C_6F_5)_2(\text{thf})_2$] (0.06 g, 0.10 mmol) for **8** (molar ratio 1:1). They were obtained as yellow solids.

7: (0.13 g, 78%). – $C_{64}H_{60}Cl_8F_{20}Ir_4Pt_2$ (2651.86): calcd. C 28.99, H 2.28; found C 28.71, H 2.45. – IR: $\tilde{\nu}$ = 810 (s), 798 (s) cm^{-1} (C_6F_5) $_{x-\text{sens}}$; 290 (m), 261 (m) cm^{-1} (M–Cl). – $^1\text{H NMR}$ ($[D_6]$ acetone): at 20 °C: δ = 1.77 (s, Cp*). – $^{19}\text{F NMR}$ ($[D_6]$ acetone): at 20 °C: δ = –167.89 (m, 8 F_m), –166.91 (t, 4 F_p), –117.47 (d, $^3J_{Pt-F}$ = 526.4, 8 F_o). – ES(+) MS: m/z (%) = 761 (100) [$Ir_2Cp^*_2Cl_3^+$]. – ES(–) MS: m/z (%) = 565 (42) [$Pt(C_6F_5)_2Cl^-$].

8: (0.1 g, 79%). – $C_{64}H_{60}Cl_8F_{20}Ir_4Pd_2$ (2474.52): calcd. C 31.07, H 2.44; found C 30.86, H 2.08. – IR: $\tilde{\nu}$ = 796 (s), 782 (s) cm^{-1} (C_6F_5) $_{x-\text{sens}}$; 287 (m), 261 (m) cm^{-1} (M–Cl). – $^1\text{H NMR}$ ($[D_6]$ acetone): at 20 °C: δ = 1.77 (s, Cp*). – $^{19}\text{F NMR}$ ($[D_6]$ acetone): at 20 °C: δ = –166.81 (m, 8 F_m), –165.29 (t, 4 F_p), –113.28 (d, 8 F_o). – ES(+) MS: m/z (%) = 761 (100) [$Ir_2Cp^*_2Cl_3^+$]. – ES(–) MS: m/z (%) = 477 (42) [$Pd(C_6F_5)_2Cl^-$].

Complexes **7** and **8** could also be obtained, albeit in lower yields (0.05 g, 46% for **7**; 0.04 g, 31% for **8**, based on Ir), by carrying out the reactions starting from [$IrCp^*Cl_2$]₂ (0.07 g, 0.09 mmol) and [$cis\text{-Pt}(C_6F_5)_2(\text{thf})_2$] (0.12 g, 0.18 mmol) for **7** and [$IrCp^*Cl_2$]₂ (0.08 g, 0.10 mmol) and [$cis\text{-Pd}(C_6F_5)_2(\text{thf})_2$] (0.12 g, 0.20 mmol) for **8** (molar ratio 1:2), following the same procedure as described for **5**.

Synthesis of $[(PEt_3)Cp^*M(\mu\text{-}1\kappa^C:\eta^2\text{-}C\equiv CPh)_2M''_2(\mu\text{-}4\kappa^C:\eta^2\text{-}C\equiv CPh)_2Pt(C_6F_5)_2]$ ($M = Rh$, $M'' = Cu$ **9, $M'' = Ag$ **10**; $M = Ir$, $M'' = Cu$ **11**, $M'' = Ag$ **12**):** An orange solution of $[(PEt_3)Cp^*Rh(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ (**1**) (0.15 g, 0.16 mmol) in acetone (10 mL) was treated with $[CuC\equiv CPh]_x$ (0.26 g, 1.58 mmol) and the mixture was stirred for 2 h. The resulting yellow suspension was concentrated to dryness, the solid residue was extracted with CH_2Cl_2 (30 mL), and the extract was filtered through Celite to eliminate the excess $[CuC\equiv CPh]_x$ and the $CuCl$ formed. The resulting yellow solution was concentrated to dryness and the residue was treated with cold Et_2O (5 mL) to yield complex **9** as a yellow solid. Complexes **10–12** were similarly prepared, also as yellow solids. In the case of complex **10**, the pale-brown solid thus obtained was recrystallized from acetone/ Et_2O to give **10** as a pure yellow solid; in the case of complex **12**, the solid residue was treated with acetone instead of diethyl ether. Reagents and quantities used: **1** (0.15 g, 0.16 mmol) and $[AgC\equiv CPh]_x$ (0.15 g, 0.72 mmol) for **10**; $[(PEt_3)Cp^*Ir(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ (**3**) (0.16 g, 0.15 mmol) and $[CuC\equiv CPh]_x$ (0.11 g, 0.69 mmol) for **11**; **3** (0.20 g, 0.19 mmol) and $[AgC\equiv CPh]_x$ (0.17 g, 0.81 mmol) for **12**.

9: (0.17 g, 75%). – $C_{60}H_{50}Cu_2F_{10}PpPtRh$ (1417.13): calcd. C 50.86, H 3.56; found C 50.44, H 3.38. – IR: $\tilde{\nu}$ = 2009 (s br), 1969 (sh) cm^{-1} ($C\equiv C$); 797 (s), 778 (s) cm^{-1} (C_6F_5) $_{x-\text{sens}}$. – $^1\text{H NMR}$ ($CDCl_3$): at 20 °C: δ = 0.91 (m, 9 H, CH_3 , PEt_3), 1.89 (m, 6 H, CH_2 , PEt_3), 2.00 (d, $^4J_{P-H}$ = 1.7, 15 H, Cp*), 7.16 (m, 20 H, Ph). – $^{19}\text{F NMR}$ ($CDCl_3$): at 20 °C: δ = –166.06 (m, 4 F_m), –164.85 (t, 2 F_p), –116.10 (dd, $^3J_{Pt-F}$ = 376.1, 4 F_o). – $^{31}\text{P NMR}$ ($CDCl_3$): at 20 °C: δ = 35.88 (d, $^1J_{Rh-P}$ = 115.7). – FAB(+) MS: m/z (%) = 1417 (8) [$M^+ + 1$], 1148 (20) [$M^+ - 2 C_2Ph - Cu - 3$], 1047 (12) [$M^+ - 3 C_2Ph - Cu - 3$], 785 (23) [$(PEt_3)Cp^*Rh(C_2Ph)_3Cu_2^+$], 621 (100) [$(PEt_3)Cp^*Rh(C_2Ph)_2Cu^+$].

10: (0.05 g, 22%). – $C_{60}H_{50}Ag_2F_{10}PpPtRh$ (1505.77): calcd. C 47.86, H 3.35; found C 47.33, H 3.35. – IR: $\tilde{\nu}$ = 2053 (s br), 2020 (sh) cm^{-1} ($C\equiv C$); 797 (s), 778 (s) cm^{-1} (C_6F_5) $_{x-\text{sens}}$. – $^1\text{H NMR}$ ($CDCl_3$): at 20 °C: δ = 0.90 (m, 9 H, CH_3 , PEt_3), 1.81 (m, 6 H, CH_2 , PEt_3), 1.86 (d, $^4J_{P-H}$ = 1.7, 15 H, Cp*), 7.17, 7.05, 6.92, 6.77 (m, 20 H, Ph). – $^{19}\text{F NMR}$ ($CDCl_3$): at 20 °C: δ = –165.91 (m, 4 F_m), –164.78 (t, 2 F_p), –114.28 (d, $^3J_{Pt-F}$ = 394.9, 4 F_o). – $^{31}\text{P NMR}$ ($CDCl_3$): at 20 °C: δ = 37.18 (d, $^1J_{Rh-P}$ = 119.3). – FAB(–) MS: m/z (%) = 1786 (23) [$Pt_2(C_6F_5)_4(C_2Ph)_4Ag_3^- - 1$], 1604 (4) [$M^- + C_2Ph - 3$], 630 (24) [$Pt(C_6F_5)_2(C_2Ph)^-$], 441 (100) [$RhCp^*(C_2Ph)_2^- + 1$].

11: (0.14 g, 61%). – $C_{60}H_{50}Cu_2F_{10}IrPpPt$ (1506.44): calcd. C 47.84, H 3.34; found C 47.43, H 3.17. – IR: $\tilde{\nu}$ = 2006 (s), 1969 (s) cm^{-1} ($C\equiv C$); 798 (s), 778 (s) cm^{-1} (C_6F_5) $_{x-\text{sens}}$. – $^1\text{H NMR}$ ($CDCl_3$): at 20 °C: δ = 0.86 (m, 9 H, CH_3 , PEt_3), 1.89 (m, 6 H, CH_2 , PEt_3), 2.06 (s, 15 H, Cp*), 7.16–7.08 (m, 20 H, Ph). – $^{19}\text{F NMR}$ ($CDCl_3$): at 20 °C: δ = –165.95 (m, 4 F_m), –164.89 (t, 2 F_p), –115.82 (d, $^3J_{Pt-F}$ = 378.4, 4 F_o). – $^{31}\text{P NMR}$ ($CDCl_3$): at 20 °C: δ = –7.57 (s). – FAB(+) MS: m/z (%) = 1507 (4) [$M^+ + 1$], 1405 (10) [$M^+ - C_2Ph$], 1337 (6) [$M^+ - C_6F_5 - 2$], 1238 (18) [$M^+ - C_2Ph - C_6F_5$], 711 (80) [$Pt(C_6F_5)_2Cu(PEt_3)$], 593 (82) [$Pt(C_6F_5)_2Cu$], 463 (100) [$Pt(C_6F_5)$].

12: (0.20 g, 66%). – $C_{60}H_{50}Ag_2F_{10}IrPpPt$ (1595.09): this complex crystallizes with a $1/2$ molecule of CH_2Cl_2 , as observed by $^1\text{H NMR}$ in $CDCl_3$. $C_{60}H_{50}Ag_2F_{10}IrPpPt\cdot 0.5CH_2Cl_2$ requires C 44.38, H 3.14; found C 44.29, H 3.44. – IR: $\tilde{\nu}$ = 2070 (m), 2036 (m) cm^{-1} ($C\equiv C$); 797 (m), 777 (m) cm^{-1} (C_6F_5) $_{x-\text{sens}}$. – $^1\text{H NMR}$ ($CDCl_3$): at 20 °C: δ = 0.88 (m, 9 H, CH_3 , PEt_3), 1.86 (m, 6 H, CH_2 , PEt_3), 1.94 (s, 15 H, Cp*), 5.33 (s, CH_2Cl_2), 7.14, 7.04, 6.90, 6.77 (m, 20 H, Ph). – $^{19}\text{F NMR}$ ($CDCl_3$): at 20 °C: δ = –165.87 (m, 4 F_m), –164.76 (t, 2 F_p), –114.34 (d, $^3J_{Pt-F}$ = 387.3, 4 F_o). – $^{31}\text{P NMR}$ ($CDCl_3$): at 20 °C: δ = –5.4 (s). – FAB(+) MS: m/z (%) = 1159 (9) [$(PEt_3)Cp^*Ir(C_2Ph)_3Ag_2Pt^+$], 965 (11) [$(PEt_3)Cp^*Ir(C_2Ph)_3Ag_2^+ - 1$], 846 (15) [$Cp^*Ir(C_2Ph)_3Ag_2^+ - 1$], 755 (55) [$(PEt_3)Cp^*Ir(C_2Ph)_2Ag^+$], 637 (100) [$Cp^*Ir(C_2Ph)_2Ag^+$].

X-ray Crystal Structure Determinations: Suitable crystals of **1**· Me_2CO , **6**, and **9**· CH_2Cl_2 were obtained by slow diffusion of hexane into acetone (**1**, **6**) or CH_2Cl_2 (**9**) solutions of these complexes at –30 °C. Relevant crystal data are listed in Table 5. Intensity data for **1**· Me_2CO and **6** were collected on a Siemens P4 four-circle diffractometer and cell constants were calculated from 30 reflections (**1**· Me_2CO) or 52 reflections (**6**) with 2θ angles ranging from 24 to 26°. Intensity data for **9**· CH_2Cl_2 were collected on a Siemens/STOE AED4 four-circle diffractometer and cell constants were refined from 2θ values of 36 reflections ($22.5 < 2\theta < 31.7^\circ$). An absorption correction based on azimuthal data was applied; transmission coefficients were in the range 1.000 to 0.677

Table 5. Crystal data and structure refinement parameters for **1**·Me₂CO, **6**, and **9**·CH₂Cl₂ ($wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum wF_o^4$)^{0.5}; $R1 = \sum|F_o| - |F_c|/\sum|F_o|$)

| | 1 ·Me ₂ CO | 6 | 9 ·CH ₂ Cl ₂ |
|--|--|---|---|
| Empirical formula | C ₂₈ H ₃₀ Cl ₂ F ₁₀ PPtRh·Me ₂ CO | C ₆₄ H ₆₀ Cl ₈ F ₂₀ Pd ₂ Rh ₄ | C ₆₀ H ₅₀ Cu ₂ F ₁₀ PPtRh·CH ₂ Cl ₂ |
| Molecular mass | 1014.47 | 2117.16 | 1501.98 |
| Temperature [K] | 200 | 200 | 173 |
| Wavelength [Å] | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Orthorhombic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>Pca</i> 2 ₁ | <i>P</i> $\bar{1}$ |
| <i>a</i> [Å] | 10.439(1) | 14.820(5) | 10.963(3) |
| <i>b</i> [Å] | 14.611(1) | 17.993(6) | 13.052(4) |
| <i>c</i> [Å] | 11.285(1) | 28.296(9) | 20.643(6) |
| α [deg] | 90 | 90 | 93.44(2) |
| β [deg] | 93.15(1) | 90 | 99.29(2) |
| γ [deg] | 90 | 90 | 106.03(2) |
| Volume [Å ³] | 1718.6(3) | 7545(4) | 2784.7(13) |
| <i>Z</i> | 2 | 4 | 2 |
| Density (calcd.) [g/cm ³] | 1.960 | 1.864 | 1.791 |
| Absorption coeff. [mm ⁻¹] | 4.827 | 1.692 | 3.747 |
| <i>F</i> (000) | 984 | 4128 | 1476 |
| Crystal dimensions [mm] | 0.52 × 0.50 × 0.36 | 0.48 × 0.44 × 0.24 | 0.30 × 0.23 × 0.19 |
| θ range [°] | 2.28 to 24.00 | 2.26 to 25.01 | 2.01 to 25.00 |
| Index ranges | -1 ≤ <i>h</i> ≤ 11 -1 ≤ <i>k</i> ≤ 16 -12 ≤ <i>l</i> ≤ 12 | -1 ≤ <i>h</i> ≤ 17 -1 ≤ <i>k</i> ≤ 21 -1 ≤ <i>l</i> ≤ 33 | 0 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 14 -24 ≤ <i>l</i> ≤ 24 |
| Reflections collected | 3582 | 8134 | 10352 |
| Independent reflections | 2802 [<i>R</i> (int) = 0.0234] | 7058 [<i>R</i> (int) = 0.0423] | 9795 [<i>R</i> (int) = 0.0374] |
| Refinement method | | Full-matrix least-squares on <i>F</i> ² | |
| Data/restraints/parameters | 2763/0/226 | 6587/1/884 | 9792/2/737 |
| Goodness-of-fit on <i>F</i> ² | 1.080 | 1.025 | 1.017 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> 1 = 0.0239 <i>wR</i> 2 = 0.0585 | <i>R</i> 1 = 0.0380 <i>wR</i> 2 = 0.0682 | <i>R</i> 1 = 0.0464 <i>wR</i> 2 = 0.0893 |
| <i>R</i> indices (all data) | <i>R</i> 1 = 0.0274 <i>wR</i> 2 = 0.0643 | <i>R</i> 1 = 0.0714 <i>wR</i> 2 = 0.1858 | <i>R</i> 1 = 0.0935 <i>wR</i> 2 = 0.1119 |
| Largest diff. peak and hole [e ⁻ ·Å ⁻³] | 0.581 and -1.080 | 0.562 and -0.749 | 1.86 and -0.81 |

(**1**·Me₂CO), 0.974 to 0.704 (**6**), and 1.000 to 0.669 (**9**·CH₂Cl₂). The structures were solved by Patterson (**1**, **9**) or direct (**6**) methods and refined against *F*² using the program SHELXL-93.^[27] All non-hydrogen atoms were assigned anisotropic displacement parameters and were refined without positional constraints, except for the disordered carbon atoms of one of the ethyl groups of the PEt₃ ligand in **9**·CH₂Cl₂ (see below), for which the interatomic distances were restrained to be 1.54 Å. A phenyl ring of one phenylacetylide ligand was found to be disordered over two positions, which were refined with partial occupancy factors of 0.5/0.5. One methyl carbon atom of the PEt₃ ligand was found to be disordered over two positions, which were refined with partial occupancy factors of 0.67/0.33. In all three structures, all hydrogen atoms were constrained to idealized geometries and were assigned a refined isotropic displacement parameter equal to 1.2 times that of their parent C atoms (1.5 times for methyl hydrogen atoms). Complex **1**·Me₂CO has a symmetry plane, and so some atoms lying in certain positions were refined at half-occupancy. The crystal of **6** is a racemic twin, with a Flack parameter of 0.49(9).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151398 (**1**·Me₂CO), -151399 (**6**), and -151400 (**9**·CH₂Cl₂). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax. (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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