Oxidative Addition Reactions to Novel Heterotrinuclear Iridium Complexes with Mixed Bridging Ligands. Crystal Structure of [{Ir(μ-pz)(μ-S^{t}Bu)I$_2$(CO)[P(OMe)$_3$]}$_2$Pd]

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The formation and properties of trinuclear heterobridged complexes of general formula [{Ir(μ-pz)(μ-S^{t}Bu)L$_2$}$_2$-Pd] [L$_2$ = cycloocta-1,5-diene **1**, (CO)$_2$ **2**, (CO)[P(OMe)$_3$] **3**; pz = pyrazolate] are reported. Complex **3** reacts with methyl iodide or mercury(II) iodide to give compounds [{Ir$_2$(μ-pz)$_2$(μ-S^{t}Bu)$_2$I(X)(CO)$_2$[P(OMe)$_3$]$_2$}Pd] [X = Me (**4**) I (**5**)]. Compound **5** undergoes a further oxidative addition with I$_2$ to form [{Ir(μ-pz)(μ-S^{t}Bu)-I$_2$(CO)[P(OMe)$_3$]}$_2$Pd], **6**. Compound **6** can be also obtained by direct addition of iodine to complex **3** in a 2:1 molar ratio. The molecular structure of compound **6** has been determined by X-ray diffraction methods. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with a = 8.763(1) Å, b = 12.023(2) Å, c = 12.713-(2) Å, α = 102.086(6)°, β = 94.108(7)°, γ = 109.174(8)°, and Z = 1. Refinement by full-matrix least-squares techniques gave final R = 0.0322. Complex **6** is trinuclear with two octahedral "IrI$_2$(CO)[P(OMe)$_3$]" moieties symmetrically connected to a central square-planar Pd atom bridged through the nitrogens of a pyrazolate group and the S atom of a 2-methyl-2-propanethiolate ligand.

Introduction

One of the most interesting current goals in organometallic and coordination chemistry is the synthesis of polynuclear transition metal complexes in which the metals are held at specific distances from each other. These systems may give rise to distinct reactivity from their monometallic analogues.[1,2]

During the last few years there has been increasing interest in binuclear complexes containing rhodium or iridium centers in close proximity. Among those, we have achieved the synthesis of binuclear complexes containing an azolate (az) and a 2-methyl-2-propanethiolate group as bridging ligands. Controlled extension of the M(μ-pz)(μ-S^{t}Bu)M core to form well defined tri- or tetranuclear compounds constitutes an attractive area of research.[3−8]

Very recently we have been involved in the preparation of homo and heterotrinuclear rhodium complexes containing the metallocycles Rh(μ-pz)(μ-L)M(μ-pz)(μ-L)Rh (M = Pd; L = pz, S^{t}Bu).[9,10] In this context, we have described a *cis*-alkyl migration process which leads to the isolation of the [{Rh(μ-pz)(μ-S^{t}Bu)I(COMe)[P(OMe)$_3$]}$_2$Pd] derivative.[11]

Our interest in this area is focused on proposing an easy method for building a multinuclear framework with the possibility of varying the metal centers and their environments. We therefore sought to extend the chemistry of the heterotrinuclear rhodium complexes Rh(μ-pz)(μ-L)M(μ-pz)(μ-L)Rh to those of iridium, anticipating that a broader range in reactivities may be observed.

The present investigation was undertaken in order to explore the reactivity of the new trinuclear iridium complexes [{Ir(μ-pz)(μ-S^{t}Bu)L}$_2$Pd] (L = (CO)$_2$, (CO)[P(OMe)$_3$]). The structural characterization of [{Ir(μ-pz)(μ-S^{t}Bu)I$_2$(CO)[P(OMe)$_3$]}$_2$Pd] is also reported.

Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). Purification was achieved by dissolving the complex in an appropiate solvent, filtering the solution through kieselguhr, adding a solvent in which the product is insoluble, and reducing the volume in vacuo to induce precipitation. [Ir(acac)(COD)][12] and [PdCl$_2$(Hpz)$_2$][9] were prepared according to literature methods. Solvents were purified according to standard procedures and distilled under nitrogen prior to use. All other reagents were purchased from Aldrich and used as received. Solution infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were carried out in CDCl$_3$ solution at room temperature on a Varian XL 300 spectrometer, with J values measured in Hz. ^{31}P chemical shifts are positive downfield from external 85% H$_3$PO$_4$ in D$_2$O. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser.

Preparation of [{Ir(μ-pz)(μ-S^{t}Bu)(COD)}$_2$Pd] (1). To a solution of [{Ir(μ-pz)(μ-Cl)(COD)}$_2$Pd] (prepared "in situ" by reaction of [Ir-(acac)(COD)] (500 mg, 1.25 mmol) with [PdCl$_2$(Hpz)$_2$] (196 mg, 0.620 mmol) in acetone (20 mL)) was added a mixture of HS^{t}Bu (141 μL, 1.25 mmol) and KOH (1.25 mmol) in methanol. The resulting red suspension was stirred for 2 h at room temperature. The evaporation of the solvents and addition of methanol (5 mL) gave a red-orange

® Abstract published in *Advance ACS Abstracts,* December 1, 1994.
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solid which was separated by filtration. The compound was purified by recrystallization from dichloromethane/methanol (618 mg, 90%). Anal. Calcd for $C_{30}H_{48}N_4Ir_2PdS_2$: C, 35.33; H, 4.74; N, 5.49. Found: C, 35.10; H, 4.60; N, 5.39. ^1H NMR (CDCl$_3$): δ 1.17 (s, S^{t}Bu), 3.80 (m, COD), 4.20 (m, COD), 6.10 (vt, $^3J_{HH}$ 1.8, H^4 pz), 7.25 (b, H^3 pz), 7.81 (d, $^3J_{HH}$ 1.8, H^5 pz).

Preparation of [{Ir(μ-pz)(μ-S^{t}Bu)(CO)$_2$}$_2$Pd] (2). Carbon monoxide was bubbled through a solution of complex 1 (153 mg, 0.150 mmol) in dichloromethane (10 mL), for 15 min, to give a yellow suspension. Evaporation of the solvent to dryness and addition of hexane (10 mL) caused the precipitation of a yellow solid which was filtered off and recrystallized from dichloromethane/hexane (75 mg, 55%). Anal. Calcd for $C_{18}H_{24}N_4Ir_2O_4PdS_2$: C, 23.62; H, 2.64; N, 6.12. Found: C, 23.54; H, 2.43; N, 6.25. IR (cm^{-1}, CH$_2$Cl$_2$): ν(CO) 2060, 1990. ^1H NMR (CDCl$_3$): δ 1.24 (s, S^{t}Bu), 6.20 (vt, $^3J_{HH}$ 2.2, H^4 pz), 7.82 (d, $^3J_{HH}$ 2.2, H^3 pz), 8.07 (b, H^5 pz).

Preparation of [{Ir(μ-pz)(μ-S^{t}Bu)(CO)[P(OMe)$_3$]}$_2$Pd] (3). A stoichiometric amount of trimethyl phosphite (47 μL, 0.400 mmol) was added to a suspension of [{Ir(μ-pz)(μ-S^{t}Bu)(CO)$_2$}$_2$Pd] (2) (183 mg, 0.200 mmol) in dichloromethane (10 mL), and the resulting yellow solution was stirred for 20 min. Concentration of the solvent to 1 mL and addition of diethyl ether (2 mL) and then hexane (10 mL) gave a yellow solid which was filtered off and recrystallized from dichloromethane/diethyl ether (183 mg, 82%). Anal. Calcd for $C_{22}H_{42}N_4Ir_2O_8P_2PdS_2$: C, 23.86; H, 3.82; N, 5.06. Found: C, 23.75; H, 4.00; N, 4.98. IR (cm^{-1}, CH$_2$Cl$_2$): ν(CO) 1990. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 93.6 (s). ^1H NMR (CDCl$_3$): δ 1.20 (s, S^{t}Bu), 3.66 (d, $^3J_{PH}$ 12.4, P(OMe)$_3$), 6.08 (vt, $^3J_{HH}$ 2.2, H^4 pz), 7.78 (b, H^3 pz), 8.14 (b, H^5 pz).

Preparation of [{Ir$_2$(μ-pz)$_2$(μ-S^{t}Bu)$_2$I(Me)(CO)$_2$[P(OMe)$_3$]$_2$}Pd] (4). MeI (5.6 μL, 0.09 mmol)) was added to a solution of complex [{Ir(μ-pz)(μ-S^{t}Bu)(CO)[P(OMe)$_3$]}$_2$Pd] (3) (100 mg, 0.090 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 6 h while the color changed from yellow to orange. Then the solvent was removed under reduced pressure to 1 mL. Addition of diethyl ether (3 mL) and hexane (5 mL) afforded a yellow solid which was separated by filtration and recrystallized from dichloromethane/hexane (76 mg, 67%). Anal. Calcd for $C_{23}H_{45}N_4IIr_2O_8P_2PdS_2$: C, 22.11; H, 3.63; N, 4.48. Found: C, 22.21; H, 3.36; N, 4.39. IR (cm^{-1}, CH$_2$-Cl$_2$): ν(CO) 2040. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 65.8 (s), 66.1 (s). ^1H NMR (CDCl$_3$): δ 1.09 (s, S^{t}Bu), 1.40 (s, S^{t}Bu$'$), 1.85 (d, $^3J_{PH}$ 3.2, Me), 3.71 (d, $^3J_{PH}$ 11.2, P(OMe)$_3$), 3.75 (d, $^3J_{PH}$ 11.0, P(OMe)$_3$), 6.03 (vt, $^3J_{HH}$ 2.2, H^4 pz), 6.07 (vt, $^3J_{HH}$ 2.2, H^4 pz$'$), 7.67 (d, $^3J_{HH}$ 2.2, H^3 pz), 8.25 (d, $^3J_{HH}$ 2.2, H^3 pz$'$, H^5 pz), 8.32 (d, $^3J_{HH}$ 2.2, H^5 pz$'$).

Preparation of [{Ir(μ-pz)(μ-S^{t}Bu)I(CO)[P(OMe)$_3$]}$_2$Pd] (5). Solid mercury(II) iodide (41 mg, 0.090 mmol)) was added to a solution of [{Ir(μ-pz)(μ-S^{t}Bu)(CO)[P(OMe)$_3$]}$_2$Pd] (3) (100 mg, 0.090 mmol) in dichloromethane (20 mL). The solution changed from yellow to red and, after 1 h of stirring, to pale yellow with formation of metallic mercury. This suspension was filtered off through kieselguhr to remove the mercury. Then the filtrate was evaporated under vacuum and addition of diethyl ether (3 mL) and hexane (5 mL) provided a yellow solid which was filtered off and vacuum dried (106 mg, 86%). Anal. Calcd for $C_{22}H_{42}N_4I_2Ir_2O_8P_2PdS_2$: C, 19.41; H, 3.11; N, 4.11. Found: C, 19.30; H, 3.10; N, 4.09. IR (cm^{-1}, CH$_2$Cl$_2$): ν(CO) 2050. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 75.4 (s). ^1H NMR (CDCl$_3$): δ 1.27 (s, S^{t}Bu), 3.79 (d, $^3J_{PH}$ 11.6, P(OMe)$_3$), 6.05 (vt, J$_{HH}$ 2.2, H^4 pz), 7.86 (d, $^3J_{HH}$ 2.2, H^3 pz), 8.37 (d, $^3J_{HH}$ 2.2, H^5 pz).

Preparation of [{Ir(μ-pz)(μ-S^{t}Bu)I$_2$(CO)[P(OMe)$_3$]}$_2$Pd] (6). Method 1. Iodine (92 mg, 0.360 mmol) was added to a solution of [{Ir(μ-pz)(μ-S^{t}Bu)(CO)[P(OMe)$_3$]}$_2$Pd] (3) (199 mg, 0.180 mmol) in dichloromethane (15 mL). The resulting orange solution was stirred at room temperature. After 30 min. the IR spectrum revealed the absence of starting material. Concentration of the solvent (1 mL) and addition of diethyl ether (3 mL) followed by hexane (5 mL) gave an orange solid which was filtered off and recrystallized from dichloromethane/hexane (254 mg, 87%). Anal. Calcd for $C_{22}H_{42}N_4I_4Ir_2O_8P_2PdS_2$: C, 16.36; H, 2.62; N, 3.47. Found: C, 16.30; H, 2.42; N, 3.41. IR (cm^{-1}, CH$_2$Cl$_2$): ν(CO) 2080. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 52.9 (s). ^1H NMR (CDCl$_3$): δ 1.36 (s, S^{t}Bu), 3.76 (d, $^3J_{PH}$ 11.3, P(OMe)$_3$), 6.06 (vt, $^3J_{HH}$ 2.2, H^4 pz), 8.22 (d, $^3J_{HH}$ 2.2, H^3 pz), 8.34 (d, $^3J_{HH}$ 2.2, H^5 pz).

Table 1. Crystallographic Data for 6·2CHCl$_3$

chem formula	$C_{24}H_{44}Cl_6L_4Ir_2N_4O_8P_2PdS_2$
fw	1853.88
temp, K	173.0(2)
space group	$P\bar{1}$
a, Å	8.763(1)
b, Å	12.023(2)
c, Å	12.713(2)
α, deg	102.086(6)
β, deg	94.108(7)
γ, deg	109.174(8)
V, Å^3	1222.6(3)
Z	1
ϱ(calcd), g cm^{-3}	2.518
λ (Mo Kα), Å	0.710 73
μ, mm^{-1}	8.84
$R(F)$ [$F^2 > 2\sigma(F^2)$]^a	0.0322
wR(F^2) [all data]^b	0.0719

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for 3502 observed references. ^{b} wR(F^2) $= (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.

Method 2. A stoichiometric amount of iodine (35.5 mg, 0.140 mmol) was added to a solution of [{Ir(μ-pz)(μ-S^{t}Bu)I(CO)[P(OMe)$_3$]}$_2$Pd] (5) (191 mg, 0.140 mmol) in dichloromethane (15 mL). Immediately the color of the solution changed from yellow to orange. The resulting solution was stirred for 30 min. Concentration of the solvent to 1 mL and addition of diethyl ether (2 mL) and hexane (8 mL) gave an orange solid which was filtered off, washed with hexane, and vacuum dried (155 mg, 68%).

X-ray Crystallography. Orange single crystals of 6 were obtained by slow evaporation of a CHCl$_3$ solution, being selected one prismatic block of 0.30 × 0.28 × 0.12 mm. Diffraction data were collected with a Siemens AED-2 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants were obtained from the least-squares fit on the setting angles of 60 reflections in the range $20 \le 2\theta \le 40°$. Reflections with 2θ in the range $3-50°$ ($-10 \le h \le 10$; $-14 \le k \le 14$; $-15 \le l \le 6$) were measured by using the $\omega/2\theta$ scan technique and corrected for Lorentz and polarization effects. Reflections were also corrected for absorption by a empirical method[13] (12 reflections). Three standard reflections were measured approximately every hour as a check of crystal and instrument stability; no variation was observed. Other details of the data collection are given in Table 1.

The structure was solved by Patterson and difference Fourier techniques (SHELXTL-Plus)[14] and refined by full-matrix least-squares on F^2 (SHELXL93),[15] first with isotropic and then with anisotropic thermal parameters for the non-hydrogen atoms, including those atoms of the solvent. Hydrogen atoms were positioned in calculated positions, and refined riding on carbon atoms with four common isotropic parameters, one for each different ligand and one for the solvent. An extinction correction was applied.[15] The refinement converged at wR-(F^2) = 0.0719 for 252 parameters and 4318 reflections, from a total of 6857 collected and 4319 unique (R_{int} = 0.0306). The calculated weighting scheme is $1/[\sigma^2(F_o^2) + (0.0284P)^2 + 1.27P]$, where P $= (F_o^2 + 2F_c^2)/3$. Atomic and thermal parameters for the non-hydrogen atoms of the complex are collected in Table 2. Scattering factors were those taken from ref 16.

Results and Discussion

We have recently described the preparation of the heterotrinuclear rhodium(I) complex [{Rh(μ-pz)(μ-S^{t}Bu)(COD)}$_2$Pd].[10] The synthetic routes utilized can be easily extended to the preparation of iridium complexes using [Ir(acac)(COD)] (acac
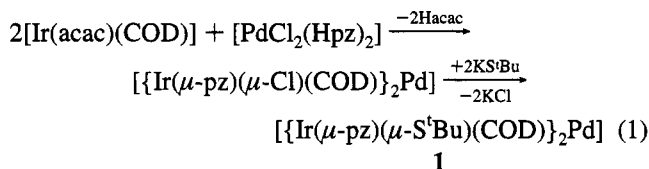
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Table 2. Fractional Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Ir, Pd, and I Atoms) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$; $\text{Å}^2 \times 10^4$ for Ir, Pd, and I Atoms) for the Non-Hydrogen Atoms of 6·2CHCl$_3$

atom	x/a	y/b	z/c	$U(eq)^a$
Ir	4728(3)	29335(2)	25681(2)	178(1)
Pd	0	50000	50000	174(3)
I(1)	−19648(6)	20703(5)	8558(4)	298(2)
I(2)	30924(6)	37968(4)	41527(4)	255(2)
S	512(2)	5008(2)	3217(2)	19(1)
P	834(2)	1092(2)	2159(2)	21(1)
N(1)	−1246(7)	2431(5)	3600(5)	20(2)
N(2)	−1484(7)	3254(5)	4431(5)	19(1)
O(1)	2729(7)	3802(5)	1010(5)	40(3)
O(2)	−815(6)	10(4)	1722(4)	26(2)
O(3)	1895(6)	954(5)	1226(4)	29(2)
O(4)	1739(6)	713(5)	3068(4)	30(2)
C(1)	1873(9)	3461(7)	1599(6)	24(3)
C(2)	−2497(8)	1384(7)	3467(6)	26(3)
C(3)	−3548(9)	1495(7)	4188(7)	32(3)
C(4)	−2864(9)	2698(7)	4783(6)	27(3)
C(5)	−1058(9)	5495(7)	2576(7)	28(3)
C(6)	−700(9)	6800(7)	3230(7)	29(3)
C(7)	−770(10)	5510(7)	1405(6)	32(3)
C(8)	−2791(9)	4704(7)	2625(7)	29(3)
C(9)	−842(10)	−1223(7)	1287(7)	32(3)
C(10)	3656(10)	1360(8)	1378(8)	44(4)
C(11)	1083(12)	519(8)	4051(7)	45(4)
Cl(1)	−6496(3)	−1382(2)	2367(2)	58(1)
Cl(2)	−5469(3)	−3242(2)	1115(2)	63(1)
Cl(3)	−4188(3)	−2192(3)	3400(2)	66(2)
C(12)	−5877(10)	−2626(8)	2392(8)	41(4)

^{a} $U(eq)$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

= acetylacetonate) and [PdCl$_2$(Hpz)$_2$] as starting materials (eq 1).

$$2[\text{Ir(acac)(COD)}] + [\text{PdCl}_2(\text{Hpz})_2] \xrightarrow{-2\text{Hacac}}$$

$$[\{\text{Ir}(\mu\text{-pz})(\mu\text{-Cl})(\text{COD})\}_2\text{Pd}] \xrightarrow[-2\text{KCl}]{+2\text{KS}^t\text{Bu}}$$

$$[\{\text{Ir}(\mu\text{-pz})(\mu\text{-S}^t\text{Bu})(\text{COD})\}_2\text{Pd}] \quad (1)$$
1

The intermediate complex [Ir(μ-pz)(μ-Cl)(COD)}$_2$Pd], shown in eq 1, has not been isolated, but its conversion into **1** is consistent with the indicated formulation. The ^{1}H NMR spectrum of complex **1** shows the presence of only one isomer in solution. Taking into account the *trans* disposition of the bridging ligands observed in the reported rhodium compound [{Rh(μ-pz)(μ-S^{t}Bu)(CO)$_2$}$_2$Pd],[10] we propose that a *trans* configuration should also be present in compound **1**.

Bubbling carbon monoxide through a dichloromethane solution of complex **1** leads to the displacement of the cyclo-octa-1,5-diene ligands and to the formation of the carbonyl derivative formulated as [{Ir(μ-pz)(μ-S^{t}Bu)(CO)$_2$}$_2$Pd] (**2**) [ν-(CO) (CH$_2$Cl$_2$): 2060 and 1990 cm^{-1}].

As expected, addition of trimethyl phosphite, in stoichiometric quantity, to a dichloromethane suspension of [{Ir(μ-pz)(μ-S^t-Bu)(CO)$_2$}$_2$Pd] (**2**) caused the evolution of carbon monoxide and formation of [{Ir(μ-pz)(μ-S^{t}Bu)(CO)[P(OMe)$_3$]}$_2$Pd] (**3**). The ^{31}P{^{1}H} NMR spectrum of compound **3** exhibits only one singlet corresponding to two equivalent phosphorus atoms (δ 93.6 ppm), and indicates the presence of symmetry in the molecule. Also, the ^{1}H NMR spectrum of this compound is in accord with this proposal.

Although a wide variety of oxidative addition reactions involving low-valent transition metal complexes have been reported, only a few metal complexes are known to undergo

simultaneous two-center oxidative addition. Most of these involve binuclear complexes in which the metal centers are held by bridging ligands.[17,18] We now report some examples of oxidative addition reactions to the heterotrinuclear complexes described above. All of these reactions involve oxidation at both iridium centers and some of them lead to metal—metal bond formation.

Reaction of Methyl Iodide with [{Ir(μ-pz)(μ-S^{t}Bu)(CO)-[P(OMe)$_3$]}$_2$Pd] (3). The addition of methyl iodide to a dichloromethane solution of compound **3** with a CH$_3$I/Ir = 1/2 molar ratio progressively causes the color of the solution to change from yellow to orange. After 5 h of stirring the infrared spectrum shows only one broad band at 2040 cm^{-1}, corresponding to terminal carbonyl ligands, while the band at 1990 cm^{-1} of the starting compound **3** has completely disappeared. These data together with the presence of two singlets (δ 66.1 and 65.8 ppm) in the ^{31}P{^{1}H} NMR spectrum of this solution, indicates that the iridium centers are inequivalent. Also the ^{1}H NMR spectrum of this compound gives key information about the molecular structure of compound **4**. It exhibits two doublets δ 3.75 ($^3J_{\text{PH}}$ 11.0 Hz) and 3.71 ($^3J_{\text{PH}}$ 11.2 Hz) corresponding to the methyl groups of two inequivalent trimethyl phosphite ligands, in accord with the ^{31}P{^{1}H} described above. At δ 1.85 ppm appears a doublet ($^3J_{\text{PH}}$ 3.2 Hz), integrating for three protons, from the methyl group coordinated to one iridium center. This type of coupling is not very usual but has also been observed in binuclear iridium(II) compounds where the CH$_3$ group and the phosphite ligands have a mutual *cis* disposition.[19]

The stoichiometry of this reaction and the described spectroscopic data agree with the addition of the methyl group to one iridium center and that of the iodide ligand to the other iridium atom leading to the formation of [{Ir$_2$(μ-pz)$_2$(μ-S^{t}Bu)$_2$I-(Me)(CO)$_2$[P(OMe)$_3$]$_2$}Pd] (**4**). The oxidative addition reaction described here can be viewed formally as a two electron oxidation of the [Ir^I(μ-pz)(μ-S^{t}Bu)Pd^{II}(μ-pz)(μ-S^{t}Bu)Ir^I] framework to form the [I-Ir^{II}(μ-pz)(μ-S^{t}Bu)Pd^{II}(μ-pz)(μ-S^{t}Bu)Ir^{II}-Me] system.

The diamagnetism observed for compound **4** is in accord with the presence of two Ir—Pd bonds. The coordination of the ligands around the Ir(II) centers is similar to that found for the metal—metal bonded Ir(II) species [Ir$_2$(μ-pz)(μ-S^{t}Bu)I(Me)-(CO)$_2${P(OMe)$_3$}$_2$] previously prepared in our laboratory.[8]

To our knowledge, up to date, only one example reported by Fackler and coworkers deals with the synchronous formation of two metal—metal bonds in a halogenation process on heterotrinuclear systems.[20]

It is noticeable that no acetyl compound has been detected in contrast with the result previously obtained in the analogous trinuclear rhodium compound which, in similar reaction conditions, leads to the rhodium(III) complex [{Rh(μ-pz)(μ-S^{t}Bu)I-(COMe)[P(OMe)$_3$]}$_2$Pd].[11]

Oxidative addition reactions of divalent mercury compounds to binuclear transition metal complexes has been scarcely explored. In this area, we have recently reported the preparation of the binuclear rhodium(II)—rhodium(II) complex [Rh$_2$(μ-S(CH$_2$)$_2$S)Cl$_2$(CO)$_2$(PPh$_3$)$_2$][21] obtained by reaction of HgCl$_2$ with [Rh$_2$(μ-S(CH$_2$)$_2$S)(CO)$_2$(PPh$_3$)$_2$]. This result seems to suggest

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Scheme 1
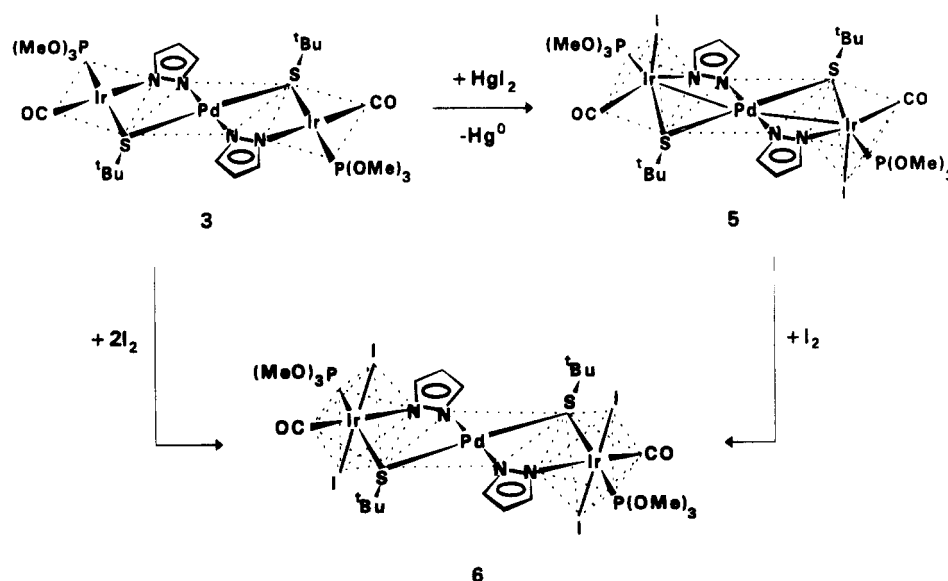
that this type of reagents may favour the special bonding situation shown in **4** to be present in related oxidation processes.

Reaction of Mercury(II) Iodide with [{Ir(μ-pz)(μ-S^{t}Bu)-(CO)[P(OMe)₃]}₂Pd] (3). Addition of mercury(II) iodide to a dichloromethane solution of [{Ir(μ-pz)(μ-S^{t}Bu)(CO)-[P(OMe)₃)]}₂Pd] (3), at room temperature, resulted in a solution color change from yellow to red and after 1 h of stirring to pale yellow and formation of metallic mercury. The pale yellow compound isolated is formulated as the iridium(II)−palladium-(II)−iridium(II) complex [{Ir(μ-pz)(μ-S^{t}Bu)I(CO)[P(OMe)₃]}₂Pd] (5) on the basis of the elemental analysis and IR and NMR spectral data. The ³¹P{¹H} spectrum of complex **5** shows a singlet at δ 75.4 ppm arising from a symmetrical compound. This fact is confirmed by the ¹H NMR spectrum which shows three pyrazolate resonances at δ 8.37, 7.86, and 6.05 ppm, one doublet from the methyl groups of the trimethyl phosphite ligands (δ 3.79) and one singlet from the 2-methyl-2-propanethiolate groups (δ 1.27). The IR spectrum exhibits a signal at 2050 cm⁻¹, corresponding to the stretching ν(CO) at a wavenumber 60 cm⁻¹ higher than that observed for compound **3**. This reaction implies the addition of one iodine atom to each iridium center with concomitant formation of two Ir−Pd bonds.

Although several symmetrical molecular structures may be proposed for compound **5** we suggest the ligand distribution shown in Scheme 1, taking into account the *trans* bridging ligand disposition observed in related bi- and trinuclear compounds³,¹⁰ with the terminal carbonyl groups in a *cis* configuration, and the sulfur atom *trans* to the trimethyl phosphite ligand. In addition, this type of configuration is confirmed by X-ray crystallography for complex **6**. (see bellow). Unfortunately crystals of **5** were unsuitable by X-ray diffraction.

Compound **5** can alternatively be obtained by addition of 2 mol of HgI₂ to compound **3**. In this case precipitation of Hg₂I₂ is observed.

This reaction was monitored at low temperature (−50 °C) by NMR spectroscopy in the hope that some intermediate species could be detected to explain the reaction mechanism. After 15 min of the addition of HgI₂ to compound **3**, the ³¹P-{¹H} NMR spectrum in deuterochloroform reveals the presence of three signals. The singlets at 77.1 and 74.6 ppm exhibit the same intensity and indicate the formation of an unsymmetrical derivative having chemically inequivalent phosphorus donor ligands. The third signal at 75.4 ppm, of low intensity,
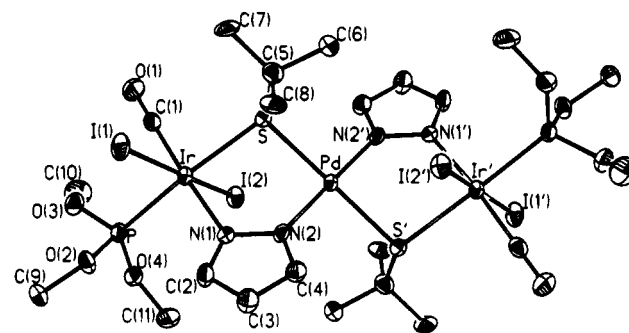

Figure 1. Structure of [{Ir(μ-pz)(μ-S^{t}Bu)I₂(CO)[P(OMe)₃]}₂Pd] (**6**). Primed atoms are related to unprimed ones by a center of symmetry.

corresponds to the symmetrical iridium(II) compound **5**. After 30 min of reaction only this last derivative remains in solution. The unsymmetrical intermediate detected may be the result of the −HgI fragment addition to one iridium center and of the −I group to the other iridium atom. Subsequent formation of metallic mercury leads to compound **5**.

Compounds **4** and **5** present a very unusual bonding situation where the iridium(II) centers are candidates to investigate further oxidative addition reactions. Effectively, compound **5** reacts with 1 mol of molecular iodine, giving [{Ir(μ-pz)(μ-S^{t}Bu)-I₂(CO)[P(OMe)₃]}₂Pd], **6**. Unfortunately compound **4** decomposes in solution after addition of iodine.

The ³¹P{¹H} NMR spectrum of compound **6** shows a singlet (δ 52.9 ppm) according with the formation of a symmetrical derivative. This data together with the presence, in the IR spectrum, of a band at 2080 cm⁻¹ (30 cm⁻¹ higher than in compound **5**) confirms the formation of the proposed iridium-(III) derivative **6**. It is worth noting that compound **6** is also obtained by direct addition of two mol of iodine to the iridium-(I) derivative [{Ir(μ-pz)(μ-S^{t}Bu)(CO)[P(OMe)₃]}₂Pd], **3** (see Scheme 1).

In order to gain additional information on the structural parameters of **6**, and specially on the intermetallic disposition, an X-ray single-crystal analysis of **6** was carried out. The crystal structure of **6** consists of trinuclear complexes together with chloroform solvent molecules. Figure 1 shows a view of the metallic complex together with the atom labeling scheme. Selected bond distances and angles are given in Table 3. The trinuclear complex has a crystallographically imposed C_i sym-

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for 6·2CHCl₃

Ir··Pd	3.6805(6)		
Ir—I(1)	2.7037(7)	Pd—S	2.343(2)
Ir—I(2)	2.7022(6)	Pd—N(2)	2.014(5)
Ir—S	2.446(2)	C(1)—O(1)	1.139(10)
Ir—P	2.297(2)	N(1)—N(2)	1.367(8)
Ir—N(1)	2.091(6)	N(1)—C(2)	1.339(8)
Ir—C(1)	1.860(8)	N(2)—C(4)	1.334(9)
I(1)—Ir—I(2)	175.00(2)	S—Pd—N(2)	88.0(2)
I(1)—Ir—S	100.88(5)	Ir—S—Pd	100.43(7)
I(1)—Ir—P	88.57(5)	Ir—S—C(5)	119.9(3)
I(1)—Ir—N(1)	89.7(2)	Pd—S—C(5)	106.5(3)
I(1)—Ir—C(1)	86.7(2)	Ir—C(1)—O(1)	178.9(7)
I(2)—Ir—S	80.73(5)	Ir—N(1)—N(2)	122.7(5)
I(2)—Ir—P	89.73(5)	Ir—N(1)—C(2)	129.0(5)
I(2)—Ir—N(1)	95.1(2)	N(2)—N(1)—C(2)	106.8(6)
I(2)—Ir—C(1)	88.6(3)	Pd—N(2)—N(1)	125.3(4)
S—Ir—P	170.42(7)	Pd—N(2)—C(4)	126.7(5)
S—Ir—N(1)	87.0(2)	N(1)—N(2)—C(4)	108.0(6)
S—Ir—C(1)	89.3(3)	N(1)—C(2)—C(3)	111.3(7)
P—Ir—N(1)	94.7(2)	C(2)—C(3)—C(4)	103.9(7)
P—Ir—C(1)	89.7(3)	N(2)—C(4)—C(3)	109.9(7)
N(1)—Ir—C(1)	174.2(3)		

metry with the Pd atom lying on the center of symmetry. The central metal is bridged to each external Ir atom by a pyrazolate group, bonded through the azolate nitrogens, and by a 2-methyl-2-propanethiolate ligand, linked to both metals through the sulphur atom. The intermetallic distance, 3.6805(6) Å, excludes any metal—metal interaction.

Each iridium completes a slightly distorted octahedral environment being bonded to two iodine atoms and to a carbonyl group and a trimethyl phosphite ligand. The deviations from the ideal octahedral coordination could be visualized through the values of the *trans* angles: 175.00(2)°, between both iodine atoms; 174.2(3)°, carbonyl—Ir—pyrazolate angle; and 170.42-(7)°, between the bridging S atom and the phosphorus of the terminal phosphite. Due to the imposed symmetry the Pd center exhibits an almost perfect square-planar coordination [S—Pd—N(2) angle 88.0(2)°]. The whole complex recalls the analogous rhodium trinuclear complex [{Rh(μ-pz)(μ-SᵗBu)(CO)₂}₂Pd], where the external metal centers coordinate two additional I atoms and one carbonyl group has changed into a P(OMe)₃ ligand.[10]

Considering the two iodide ligands *trans*-bonded on each iridium as apical positions of the octahedral coordination, the equatorial plane defined by P, C(1), S, and N(1) is twisted respect to the coordination plane of the Pd atom, giving rise to a dihedral angle of 45.1(1)°. This "step" conformation obviously reduces the steric repulsion that could be foreseen between I(1) and the thiolate methyl groups for an ideal planar conformation (see Figure 2). In accordance with this, the Ir—S—C(5) angle is significantly larger than the corresponding Pd—S—C(5) angle, 119.9(3) and 106.5(3)° respectively, confering an additional asymmetry to the thiolate bridge. The main asymmetry of the bridging ligands, shown as different M—S and M—N bond lengths, is a consequence of the different electronic environment of the two metals (octahedral vs. square-planar coordination, d⁶ vs d⁸ electronic configuration), and especially of the *trans*-situated ligands.

The Pd—S bond distance, 2.343(2) Å, is identical to that reported in the analogous [{Rh(μ-pz)(μ-SBuᵗ)(CO)₂}₂Pd] complex,[10] 2.349(2) Å, and is close to the mean value described in four-coordinated Pd complexes with bridging alkane thiolate ligands, 2.328(7) Å.[22] The Pd—N length, 2.014(5) Å, compares well with that determined in the above mentioned trinuclear
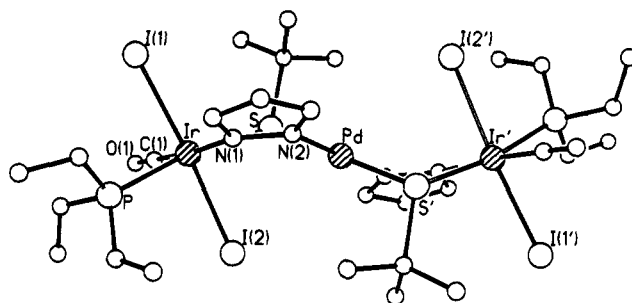
Figure 2. Alternative view of the complex [{Ir(μ-pz)(μ-SᵗBu)-I₂(CO)[P(OMe)₃]}₂Pd] (6), showing the step conformation of the metal coordination planes.

Rh—Pd—Rh complex[10] and in other related pyrazolate palladium compounds.[23-25]

Regarding the Ir coordination sphere, the Ir-donor-atom bond distances are analogous to those reported in similar dinuclear Ir(III) complexes containing pyrazolate and/or butanethiolate bridging ligands and terminal iodide, carbonyl and phosphine groups, *i.e.* [Ir₂(μ-SᵗBu)₂(μ-CO)I₂(CO)₂(PMe₃)₂],[26] [Ir₂(μ-pz)₂-(μ-CH₂)I₂(CO)₂(PPh₃)₂],[27] [Ir₂(μ-pz)(μ-SᵗBu)(μ-MeO₂CC=CCO₂-Me)I₂(CO)₂{P(OMe)₃}₂]⁴, or [Ir₂(μ-pz)(μ-SᵗBu)(μ-CH₂)I₂(CO)₂-{P(OMe)₃}₂].[8] The only noteworthy feature is the Ir—I lengths, 2.7022(6) and 2.7037(7) Å, notably shorter than those described in the previously referred complexes (mean 2.801(1) Å). However, these distances compare well with Ir—I bond distances found in mononuclear complexes where two terminal iodine atoms are coordinated in relative *trans* positions, *i.e.* 2.6954(6) and 2.6926(6) Å in AsPh₄[IrI₄(dppe)]²⁸ or 2.672(2) and 2.684-(2) Å in [IrI₂(CO)(COMe)(bipy)],[29] evincing the low *trans*-influence of the iodide ligand.

In conclusion, the heterotrinuclear heterobridged unit Ir(μ-pz)(μ-SᵗBu)Pd(μ-pz)(μ-SᵗBu)Ir has been shown to be an adequate metallic core to allow stepwise addition of electrophilic reagents allowing preparation of formally IrᴵᴵPdᴵᴵIrᴵᴵ and Irᴵᴵᴵ-PdᴵᴵIrᴵᴵᴵ complexes where formation and subsequent breaking of metal—metal bonds are observed to take place. The X-ray analysis of [{Ir(μ-pz)(μ-SᵗBu)I₂(CO)[P(OMe)₃]}₂Pd] confirmed the *trans* addition of the iodide atoms on two different metallic centers as well as the remarkable flexibility of the pyrazolate—2-methyl-2-propanethiolate bridges.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, full experimental details of the X-ray analysis and complete bond lengths and angles are available (16 pages). Ordering information is given on any current masthead page.

IC940769A

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