A New Series of Dimetallic Cationic Cyclopentadienyl-phosphine-bridged Complexes of Rhodium(II) and Iridium(II)

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The complexes $[M^I(C_5H_4PPh_2)(CO)]_2$ [M = Rh (**1a**) or Ir (**1b**)] were chemically oxidized, affording the synthesis of a novel series of cationic dimetallic bridged complexes of divalent rhodium and iridium, $[M^{II}(C_5H_4PPh_2)_2L]_2{}^{2+}$ [L = CO (**2a, 2b**), pyridine (M = Rh) (**4a**), $P(OMe)_3$ (M = Rh) (**7a**), solvent (**5a, 6a**, *etc.*)]; surprisingly, the new double-bridging system $C_5H_4PPh_2$ allows both a long metal–metal distance [4.3029(6) Å] in (**1a**) and a short metal–metal bond [2.7796(9) Å] in (**4a**) while its change of conformation leads the terminal ligand L on each metal site of (**4a**) to adopt an interesting *cisoid* mutual disposition.

Numerous complexes containing both one cyclopentadienyl and one phosphine as ancillary ligands in their co-ordination sphere have interesting properties. For instance, $M(Cp)(PR_3)H_2$ (M = Rh or Ir; Cp = $C_5H_5{}^-$ or substituted cyclopentadienyl)[1] and $Ru(Cp)(PCy_3)H_3$[2] (Cy = cyclohexyl) have interesting C–H activation behaviour and $[Ir(Cp)(PR_3)H_3]^+$ (ref. 3) and $[Ru(Cp)(PR_3)H_3]$ (ref. 4) have remarkable ^1H NMR data. The extension of such studies to related bimetallic complexes is now possible using cyclopentadienyl substituted phosphines[5] as bridging ligands.[6] We have recently shown that the dirhodium complexes $[Rh^I(C_5H_4PR_2)(CO)]_2$ (R = Ph or Me) are easily prepared but have a limited reactivity.[7] Moreover, their structures, in which a long metal–metal distance is characteristic, seem to be *a priori* unsuitable for a co-operative effect between their metallic sites. With the aim of overcoming these difficulties, we have now prepared and studied a novel series of related rhodium(II) and iridium(II) binuclear derivatives.[8]†

$[M(C_5H_4PPh_2)(CO)]_2$
(**1**)
$[M(C_5H_4PPh_2)(CO)]_2[PF_6]_2$
(**2**)
a; M = Rh
b; M = Ir

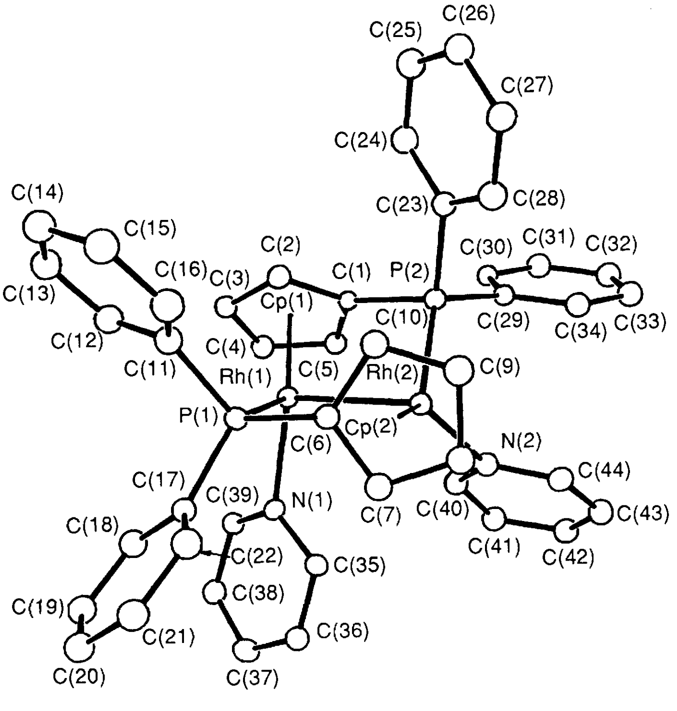

Figure 1. Molecular structure of $[Rh(C_5H_4PPh_2)(py)]_2{}^+$.

As shown by preliminary voltammetric experiments,[9] the complexes $[M(C_5H_4PPh_2)_2(CO)]_2$ [M = Rh (**1a**) or Ir (**1b**)] are easily oxidized [E_{pa} 0.167 V *vs.* standard calomel electrode (SCE) for (**1a**), 0.230 V for (**1b**) in CH_2Cl_2]. Therefore, both ferricinium tetrafluoroborate and silver hexafluorophosphate were used as oxidizing reagents. In the first case, a suspension of stoicheiometric amounts of (**1a**) and $(Cp)_2Fe^+BF_4{}^-$ in CH_2Cl_2 was stirred for 1 h, leading, after the disappearance of the initial solid reagents, to the precipitation of orange–red crystals of $[Rh(C_5H_4PPh_2)(CO)]_2[BF_4]_2$ (**2a**). Similarly, (**1b**) afforded $[Ir(C_5H_4PPh_2)(CO)]_2[BF_4]_2$ (**2b**). With $AgPF_6$, the reaction of (**1a**) [or (**1b**)] led first to a yellow intermediate precipitate (**3a**) [or (**3b**)], which was characterized by IR spectroscopy [ν_{CO} 2010 cm^{-1} (**3a**), 2013 cm^{-1} (**3b**)]. These intermediates (**3a**) [or (**3b**)] progressively transformed[10] to orange–red compounds (**2a**′) [or (**2b**′)], while a silver mirror was formed on the wall of the Schlenk tube. After recrystallization from acetone, (**2a**′) and (**2b**′) were identified as $[Rh(C_5H_4PPh_2)(CO)]_2[PF_6]_2$ (ν_{CO} 2085 cm^{-1}) and $[Ir(C_5H_4PPh_2)(CO)]_2[PF_6]_2$ (ν_{CO} 2071 cm^{-1}), respectively. The latter dicationic compounds were easily reduced to (**1a**) and (**1b**), respectively, by reaction either with zinc powder or with $LiBEt_3H$, $NaBH_4$, or KOH. In the last three cases, no reaction of the corresponding nucleophiles H^- or OH^- on the carbonyl ligands was observed.[11] By contrast, these carbonyl ligands were easily substituted by harder bases. Thus, a pyridine (py) solution of the yellow compound (**2a**) progressively turned blue and subsequent evaporation of the pyridine and washing with diethyl ether afforded the intense blue substituted derivative $[Rh(C_5H_4PPh_2)(py)]_2[BF_4]_2$ (**4a**).

The *X*-ray diffraction study‡ of this 1:2 electrolyte (**4a**) provides noteworthy information on the dicationic species. Figure 1 shows the head-to-tail disposition of the bridging ligands which is similar to that observed in (**1a**)[7a,b] but the conformation of the dimetallic complex changes drastically.

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† All compounds gave satisfactory C and H analyses and have been fully characterized spectroscopically.

‡ *Crystal data:* $C_{44}H_{38}N_2P_2Rh_2{\cdot}B_2F_8{\cdot}CH_4O$, M = 1068.2, monoclinic, space group $P2_1/n$, a = 12.896(2), b = 23.262(3), c = 16.726(2) Å, β = 107.12(2)°, U = 4795(2) Å^3, Z = 4, D_c = 1.48 g cm^{-3}, μ = 8.1 cm^{-1}. Measurements: CAD4; solution: SHELX programs. 7046 unique reflections, 4289 observed [$I > 2\sigma(I)$], number of variables: 323 (phenyl and cyclopentadienyl rings refined as isotropic rigid groups, other non-H atoms anisotropic). R = 0.042, R_w = 0.045. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of the series of dimetallic Rh^{II}–Rh^{II} and Ir^{II}–Ir^{II} complexes.[a]

Complex		$\delta(^{31}P)$[b]/ppm	J_{P-Rh}/Hz	$\delta(^{1}H)$[c]
$[Rh(CO)(C_5H_4PPh_2)]_2^{2+}[A]_2$	**(2a)**	43.2 (AA′XX′)	123.0	7.23m, 6.15m, 4.34m (8H of C_5H_4)
$[Ir(CO)(C_5H_4PPh_2)]_2^{2+}[A]_2$	**(2b)**	3.4 (s)		7.40m, 6.19m, 4.65m (8H of C_5H_4)
$[Rh(py)(C_5H_4PPh_2)]_2^{2+}[A]_2$	**(4a)**	44.2 (AA′XX′)	145.6	6.8m and 2.7m (8H of C_5H_4)
$[Rh(MeCN)(C_5H_4PPh_2)]_2^{2+}[A]_2$	**(5a)**	49.4 (AA′XX′)	148.5	7.31m, 6.83m, 5.98m, 3.02(8H of C_5H_4) 1.90s (6H of MeCN)
$[Rh\{P(OMe)_3\}(C_5H_4PPh_2)]_2^{2+}[A]_2$	**(7a)**	129.6 (ddd)[d]	248.5[f]	5.92m and 5.74m (8H of C_5H_4)
		40.3 (ddd)[e]	129.7	3.60d (J_{H-P} 12.03 Hz, 18H of Me)
$[Rh(I)(C_5H_4PPh_2)]_2$	**(8a)**	35.2 (AA′XX′)	151.0	6.7m, 6.3m, 5.8m, 3.5m (8H of C_5H_4)
$[Rh(Cl)(C_5H_4PPh_2)]_2$	**(9a)**	41.6 (AA′XX′)	151.5	6.7m, 6.3m, 5.7m, 2.7 (8H of C_5H_4)

[a] A = BF_4^-. [b] In $(CD_3)_2CO$–Me_2CO. [c] In $(CD_3)_2CO$. [d] Phosphite. [e] Phosphine. [f] J_{P1-P2} 76.5; $J_{P-P2'}$ 7.3 Hz.

Indeed, the remarkable shortening of the rhodium–rhodium distance from 4.3029(6) Å[7a,b] to 2.7796(9) Å demonstrates, as expected for a d^7–d^7 species, the formation of a metal–metal single bond which is probably the driving force of this conformational change. As a consequence, a *cisoid* mutual disposition of the pyridine ligands is observed. From this result, we assume *a priori* the same characteristic disposition in all the d^7–d^7 complexes that we prepared, namely compounds **(2a)** and **(2b)** as well as compounds prepared subsequently, **(5a)**—**(9a)**. A systematic method of preparation of these complexes has been devised starting from the solvated cationic species, $[Rh(C_5H_4PPh_2)(solv)]_2^{2+}$. Such species were produced by decarbonylation of **(2a)** using trimethylamine oxide. Thus, when acetonitrile was poured on a solid mixture of **(2a)** and $Me_3NO{\cdot}2H_2O$, a violet solution formed from which, after evaporation *in vacuo*, dissolution in dichloromethane, and precipitation by diethyl ether, the violet salt $[Rh(C_5H_4PPh_2)(MeCN)]_2[BF_4]_2$ **(5a)** was obtained.

A similar reaction was also performed in dichloromethane and the corresponding green solvated species **(6a)** was conveniently used in a one-pot process without further isolation. For instance it was easily transformed into other d^7–d^7 products, *e.g.*, $[Rh(C_5H_4PPh_2)\{P(OMe)_3\}]_2[BF_4]_2$ **(7a)** by reaction with a neutral ligand in excess, here $P(OMe_3)$. It was also easy to synthesize the red halogeno compounds $[Rh(C_5H_4PPh_2)X]_2$ [X = I**(8a)** or Cl **(9a)**] by treatment of a solution of **(6a)** in dichloromethane with the corresponding halide (KI or LiCl, respectively).

In the $^{31}P\{^{1}H\}$ NMR spectra of compounds **(2a)**, **(4a)**, **(5a)**, **(8a)**, and **(9a)** (Table 1), the occurrence of a single AA′XX′ signal clearly shows the equivalence of both phosphorus ligands and their presence on separate rhodium nuclei, in agreement with structures of the type observed for **(4a)** in the solid state. The apparent coupling constants J_{P-Rh} are in all cases smaller than for **(1a)**. The ^{1}H (Table 1) and ^{13}C NMR spectra in this series of complexes are consistent with solution structures similar to that of **(4a)** in the crystal. The ^{1}H NMR spectrum of **(5a)** in CH_2Cl_2 shows the co-ordinated acetonitrile resonance at δ 1.9, a chemical shift close to that observed (δ 1.95) in $[Pt_2H(MeCN)(Ph_2PCH_2PPh_2)_2]$[12] but different from those of $(C_5Me_5)M(MeCN)_3$ (M = Rh or Ir) (δ 2.53 and 2.76 respectively).[13]

The new type of flexibility of the C_5H_4–PR_2 double bridging system, exemplified above, may offer new perspectives in organometallic chemistry and we are currently extending our work to other metals with particular emphasis on the metal–metal bond-making and -breaking.

Received, 29th December 1989; Com. 9/05524J

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