Inorg. Chem. **1990**, *29*, 1193–1198

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Heteropolymetallic Complexes of 1,1′-Bis(diphenylphosphino)ferrocene (dppf). 5. Synthesis and Characterization of the Cationic Complexes $[M(dppf)_2]^+$ (M = Rh, Ir). Crystal and Molecular Structure of $[Ir(dppf)_2]B(C_6H_5)_4$

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Received June 7, 1989

Ferrocenylbis(phosphine) complexes of the type $[M(dppf)_2]X$ (M = Rh (**1**), Ir (**2**, **4**); dppf = 1,1′-bis(diphenylphosphino)ferrocene; X = ClO_4^-, $B(C_6H_5)_4^-$) have been prepared and characterized in solution by ^{31}P NMR investigation. The two bis(phosphines) in the cationic complex $[Rh(dppf)_2]^+$ are chemically equivalent at ambient temperature, but they exhibit AA′BB′X and A_2M_2X patterns in their ^{31}P NMR spectrum at −90 °C. These patterns are indicative of a dimeric complex, $[Rh(dppf)(\mu\text{-dppf})]_2^{2+}$ (**5**), as predominant species in solution, in equilibrium with the pentacoordinated fluxional trigonal-bipyramidal species $[Rh(dppf)_2S]^+$ (**6**), in which a solvent molecule occupies an equatorial position. A similar temperature dependence of the ^{31}P NMR spectrum is exhibited by $[Ir(dppf)_2]B(C_6H_5)_4$. This has been further characterized by single-crystal X-ray diffraction analysis. The complex crystallizes in the monoclinic system, space group *C*2/*c*, with a = 41.814 (5) Å, b = 14.886 (5) Å, c = 26.515 (5) Å, β = 94.62 (3) °, and Z = 8. In the cation $[Ir(dppf)_2]^+$, the four P atoms are directly bonded to the metal atom with Ir–P distances ranging from 2.32 to 2.39 Å. The coordination geometry around the metal center is intermediate between square planar and tetrahedral, and it reveals the largest tetrahedral distortion for a d^8 complex reported so far. Under certain conditions, the neutral cyclometalated Ir(III) complex $[Ir(dppf)(H)(Cl)]_2(\mu\text{-dppf}(-2H))$ (**3**) was isolated and spectroscopically characterized.

Introduction

Since the time of the synthesis of 1,1′-bis(diphenylphosphino)ferrocene,[1] dppf, a variety of transition-metal complexes stabilized by ferrocenyl-1,1′-bis(phosphines) have been characterized.[2] The current interest on the chemistry of these complexes stems primarily from the catalytic properties exhibited by some of them[3] and from a peculiar reactivity imparted by this ligand to Pt(II) derivatives.[4]

As a part of our studies on the synthesis of heteropolymetallic complexes, we have recently reported on a series of transition-metal complexes containing the dppf ligand.[5] Although the free ligand is centrosymmetric with the inversion center at the Fe atom,[5d] in all the X-ray structurally characterized complexes the ferrocenylbis(phosphine) is found to act as a bidentate chelating ligand. The first example of a metal complex in which the geometry of the free ligand is preserved has been only recently reported in the case of $[Mo(CO)_5]_2(\mu\text{-dppf})$,[6] and an analogous case involving copper(I) has been observed in these laboratories.[7] So far, only heteroleptic complexes of dppf have been reported in the literature, and it appeared interesting to investigate the ligating modes of dppf in expectedly "crowded" homoleptic complexes of the $[M(dppf)_n]^{m+}$ type.

We report here the synthesis and ^{31}P NMR characterization of the complexes $[M(dppf)_2]^+$ (M = Rh, Ir), as well as the crystal and molecular structure of $[Ir(dppf)_2]BPh_4$. In addition, the synthesis and spectroscopic characterization of the first example of a cyclometalated 1,1′-bis(diphenylphosphino)ferrocene complex are described.

Results

Preparation of the Compounds. The rhodium complex $[Rh(dppf)_2]BPh_4$ (**1**) can be obtained in fairly good yield from $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) by reaction of 2 equiv of ferrocenylbis(phosphine) in dichloroethane solution, at reflux temperature, according to eq 1.

$$[Rh(COD)Cl]_2 \xrightarrow[C_2H_4Cl_2]{dppf} (\text{red soln}) \xrightarrow[CH_3OH]{NaBPh_4}$$
$$\underset{\text{“red form”}}{[Rh(dppf)_2]BPh_4} \xrightarrow[\text{reflux temp}]{CH_2Cl_2/C_2H_5OH} \underset{\text{“yellow form”}}{[Rh(dppf)_2]BPh_4} \quad (1)$$

Addition of $NaBPh_4$ to the resulting solution gives rise to a brick red precipitate, which evolves, at ca. 70 °C in a few hours, to a microcrystalline yellow solid (yellow form of **1**). Dissolution of this species in dichloromethane or 1,2-dichloroethane (DCE) at room temperature, followed by precipitation with ethanol or methanol, gives a red precipitate (red form of **1**), which converts into the yellow one heating the suspension for a few minutes. The ^{31}P NMR spectra of both species dissolved in dichloromethane are identical, as are their electronic spectra. The ^1H NMR spectra of the red and yellow forms, in CD_2Cl_2 solution, are identical, the only difference being the relative intensity of the singlet at δ 3.76 attributable to the presence of 1,2-dichloroethane, the solvent used for the recrystallization. Thus, the red crystals appear to contain ca. 1.6 mol of DCE/mol of rhodium and only a small amount of the solvent appears to be present in the yellow one. On the other hand, while the infrared spectra in the 4000–550-cm^{-1} region are very similar, they turn out to be appreciably different in the 550–300-cm^{-1} range. In addition to this, the powder X-ray diffraction spectra[8] unambiguously show that the two forms are not isotypic. We tentatively propose that the red and yellow solids are dimorphic forms of the same chemical compound.

The analogous iridium complex $[Ir(dppf)_2]^+$ can be also obtained from $[IrCl(COD)]_2$, but in this case the yield is very low owing to the substantial formation of the cyclometalated Ir(III) complex **3** (see later). If $[IrCl(COT)_2]_2$ (COT = cyclooctene) is used as starting material, $[Ir(dppf)_2]^+$ is obtained in quite acceptable yield, first as the perchlorate salt **2** and, after methatetical exchange, as the tetraphenylborate derivative **4** (eq 2).

The direct reaction of dppf with $[IrCl(COD)]_2$ (in molar ratio 4:1) in toluene at reflux temperature leads to complex **3** (Figure

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$$[IrCl(COT)_2]_2 \xrightarrow{dppf,\ TlClO_4} \underset{2}{[Ir(dppf)_2]ClO_4} \xrightarrow{NaBPh_4} \underset{4}{[Ir(dppf)_2]BPh_4} \quad (2)$$

1), which is characterized by elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectroscopies. The combination of these data points to a neutral monohydrido–Ir(III) complex resulting from the intramolecular cyclometalation reaction depicted in eq 3.

$$[Ir(COD)Cl]_2 \xrightarrow[-COD]{dppf,\ toluene} \underset{3}{[Ir(dppf)(H)(Cl)]_2(\mu\text{-dppf}(-2H))} \quad (3)$$

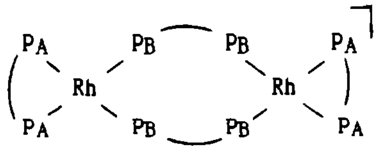
The solid-state IR spectrum of **3** exhibits a strong absorption at 2250 cm^{-1}, attributable to a terminal hydrido ligand, and a weak band at 300 cm^{-1}, in agreement with the presence of a chloride ligand coordinated to an iridium atom. The formation of an Ir–H bond is confirmed by the presence of an apparent quartet at δ −18.7 (J(PH) = 14 Hz) in the ^1H NMR spectrum. The corresponding ^{31}P NMR spectrum at 27 °C (Figure 2) displays an ABC pattern (δ: P_A −2.9, P_B −88.7, and P_C −3.5 with $J(P_AP_B)$ = 381 Hz and $J(P_CP_A) = J(P_CP_B)$ = 15.8 Hz, respectively). The high-field shift observed for one of the phosphine resonances ($\delta(P_B)$ = −88.7 vs −17.5 ppm for free dppf) suggests the presence of a diphosphine ligand bridging two octahedral [(dppf)Ir(H)Cl] moieties.[9] The iridium–hydrogen bond is interpreted as resulting from the intramolecular oxidative addition of one of the ortho C–H bonds of the phosphine phenyl substituents. As a matter of fact, ortho-metalation involving phenyl-substituted phosphines is a very common reaction in crowded iridium phosphine complexes.[10] If we assume that the hydrido ligand in **3** is trans to the chloride, as indicated by its IR and ^1H NMR data,[11] two isomeric structures can be envisaged for **3** (figure 1):

The available spectroscopic data do not allow us to discriminate between the two structures.

Discussion

^{31}P NMR Studies on $[M(dppf)_2]BPh_4$ (M = Rh, Ir). The structures of complexes **1** and **4** in solution were investigated by $^{31}P\{^1H\}$ NMR spectroscopy in CD_2Cl_2 solution. At 36.23 MHz at room temperature, complex **1** exhibits a sharp doublet centered at δ 22.2 with a Rh–P coupling constant of 144 Hz, as shown in Figure 3. As the temperature decreases, the doublet gradually broadens and eventually an AA′BB′X multiplet and a very broad doublet are obtained at −90 °C. When the same experiment is carried out at 162 MHz at −90 °C, the latter broad resonance appears as well-resolved A_2M_2X multiplets centered at δ 28.2 (J(RhP) = 134 Hz and J(PP) = 39.6 Hz) and δ 22.5 (J(RhP) = 134 Hz and J(PP) = 39.6 Hz), respectively (Figure 4).

Computer simulation of the AA′BB′X multiplet gave the parameters reported in Table I, which are consistent with the presence of a dimeric species **5** containing both chelated (P_A) and bridging (P_B) bis(phosphine) ligands.



5

The A_2M_2X pattern is attributed to the pentacoordinated species, likely the solvento complex $[Rh(dppf)_2S]^+$ (**6**), in equilibrium with the dimeric complex **5** (eq 4).

$$\underset{5}{\tfrac{1}{2}[Rh(dppf)(\mu\text{-dppf})]_2^{2+}} + S \rightleftarrows \underset{6}{[Rh(dppf)_2(S)]^+} \quad (4)$$

In fact, the ^{31}P parameters of **6** are reminiscent of those observed for $[Rh(dppp)_2]^+$, where dppp is $Ph_2P(CH_2)_3PPh_2$, in solution of acetone at −80 °C.[12] However, in that case the trigonal-bipyramidal complex, in which a solvent molecule occupies an equatorial position, is the *only* species detected in acetone or dichloromethane solution. On the contrary, our data indicate that, in CD_2Cl_2 solution at −90 °C, $[Rh(dppf)_2]^+$ does maintain a tetracoordinated geometry, through the formation of the dimeric

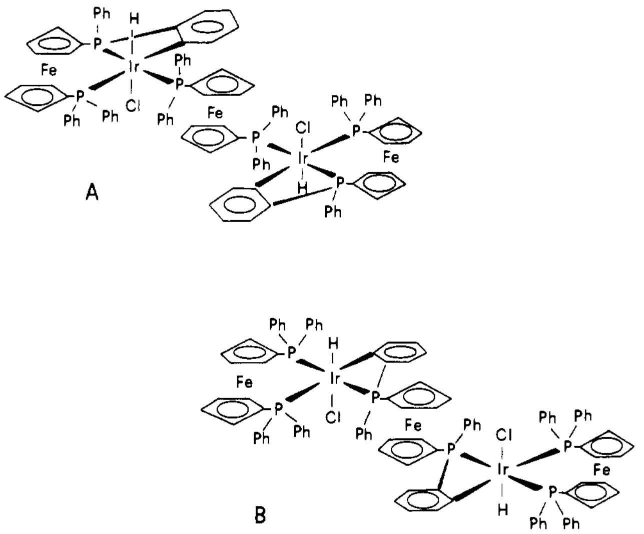


Figure 1. Proposed structures for **3**.

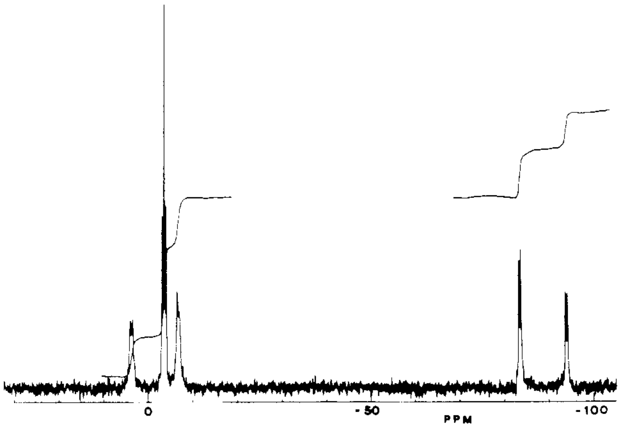
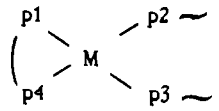


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $[(dppf)Ir(H)(Cl)]_2(\mu\text{-dppf}(-2H))$ (**3**) in CD_2Cl_2 at 27 °C.

Table I. ^{31}P NMR Data for $[M(dppf)(\mu\text{-dppf})]_2^{2+}$ in CD_2Cl_2 at −90 °C (M = Rh (**5**), Ir (**7**))



chem shift, ppm		coupling const, Hz	
		M = Rh	
$P^1 = P^4$	31.8	1,2 = 3,4	−36.5
$P^2 = P^3$	9.3	1,3 = 2,4	281.6
		1,4	−37.4
		2,3	−45.9
		Rh,1 = Rh,4	134.8
		Rh,2 = Rh,3	150.5
		M = Ir	
$P^1 = P^4$	15.21	1,2 = 3,4	−30.2
$P^2 = P^3$	−2.58	1,3 = 2,4	289.1
		1,4 = 2,3	−23.5

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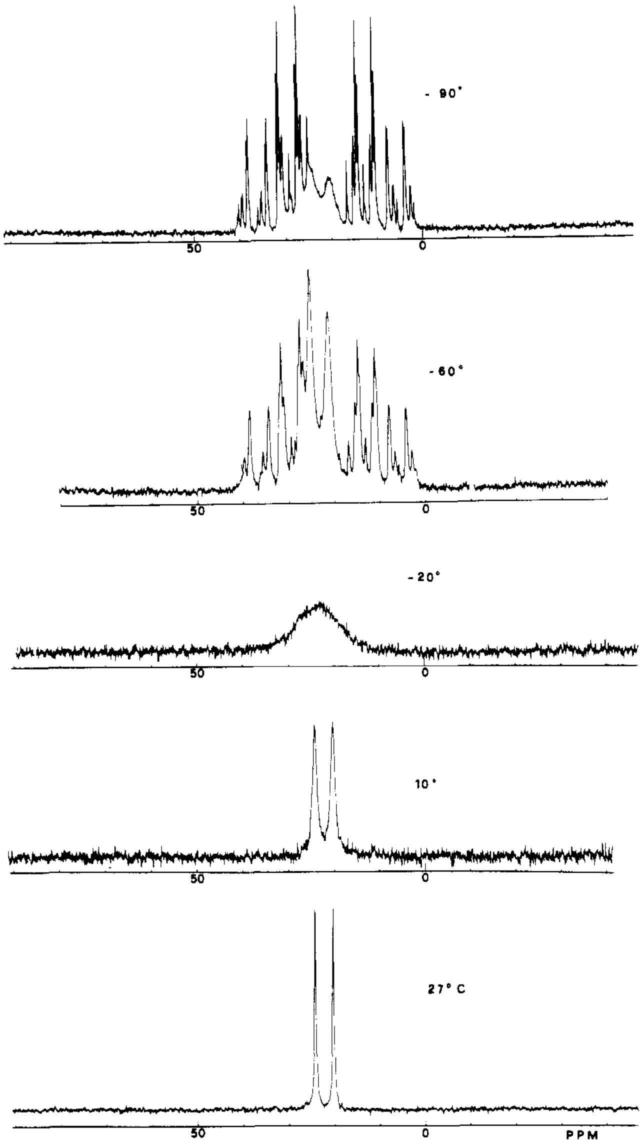

Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[Rh(dppf)_2]BPh_4$ in CD_2Cl_2 solution at 36.23 MHz.

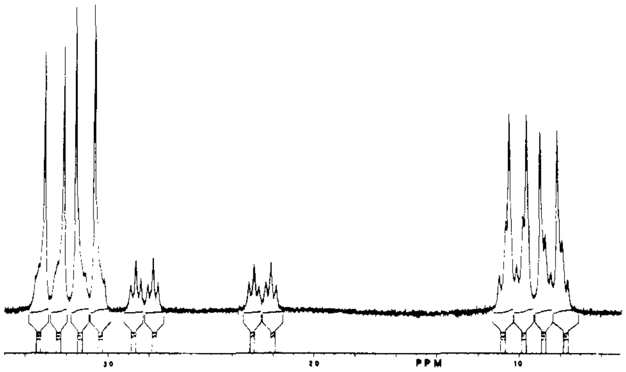

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of $[Rh(dppf)_2]BPh_4$ (**1**) in CD_2Cl_2 solution at –90 °C and 162 MHz.

species **5**, and that the coordination of the solvent molecule forming the pentacoordinated species accounts only for 15% of the total rhodium concentration (Figure 4).

Investigation of the solvolytic equilibrium (4) in more strongly coordinating solvents such as tetrahydrofuran or acetone was prevented by solubility problems.

The chemical equivalence of the phosphine ligands resulting from the ^{31}P NMR analysis of **1** at room temperature is interpreted as being due to the quantitative conversion of **5** into **6** and to a rapid interconversion of the mutual positions of the donating atom pairs between the equatorial and axial ones in the pentacoordinate complex **6**. Similar fluxional behavior has been observed, and identically explained, for the related complex $[Rh(dppp)_2]^+$ in acetone solution at room temperature.[12]

Table II. Crystal and Intensity Data for $[Ir(dppf)_2]BPh_4$ (**4**)

formula: $C_{92}H_{76}BFe_2IrP_4$
fw 1620
system: monoclinic
space group: $C2/c$
a = 41.814 (5) Å
b = 14.886 (5) Å
c = 26.515 (5) Å
β = 94.62 (3)°
V = 16450 Å^3
D_c = 1.33 g/cm^3
Z = 8
μ(Mo Kα) = 23 cm^{-1}
λ(Mo Kα) = 0.7107 Å
scan mode: $\theta/2\theta$
scan speed: 2° min^{-1}
cryst size: max 0.2 mm
no. of recorded reflns: 9391
no. of obsd reflns ($I > 3\sigma(I)$): 5393
θ_{max} = 25°
corrections applied: Lp, absorption[19]
structure factors: ref 18
refinement: full-matrix least squares
R factor: 8.4%

Table III. Selected Bond Lengths and Contact Distances (Å) and Angles (deg) of **4** (Esd's in Parentheses)

Ir–P1	2.317 (6)	Fe1···Cp1[a]	1.661 (3)
Ir–P2	2.389 (5)	Fe1···Cp2[a]	1.667 (3)
Ir–P3	2.337 (5)	Fe2···Cp3[a]	1.655 (3)
Ir–P4	2.343 (6)	Fe2···Cp4[a]	1.659 (3)
P1–C1	1.86 (2)	P3–C35	1.83 (2)
P1–C7	1.85 (1)	P3–C41	1.84 (2)
P1–C13	1.83 (2)	P3–C47	1.89 (2)
P2–C18	1.85 (2)	P4–C52	1.83 (2)
P2–C23	1.84 (2)	P4–C57	1.84 (2)
P2–C29	1.84 (1)	P4–C63	1.83 (2)
B–C69	1.72 (3)	B–C81	1.71 (4)
B–C75	1.63 (4)	B–C87	1.70 (3)
P1···P2	3.470 (8)	P1···P4	3.456 (8)
P3···P4	3.412 (8)	P2···P3	3.575 (7)
P1–Ir–P2	95.0 (2)	Ir–P2–C18	126.5 (5)
P1–Ir–P3	140.6 (2)	Ir–P2–C23	104.7 (5)
P1–Ir–P4	95.7 (2)	Ir–P2–C29	121.9 (5)
P2–Ir–P3	98.3 (2)	Ir–P3–C35	105.6 (5)
P2–Ir–P4	145.9 (2)	Ir–P3–C41	124.5 (4)
P3–Ir–P4	93.6 (2)	Ir–P3–C47	122.6 (6)
Ir–P1–C1	121.6 (5)	Ir–P4–C52	119.7 (5)
Ir–P1–C7	112.5 (5)	Ir–P4–C57	112.2 (5)
Ir–P1–C13	114.0 (5)	Ir–P4–C63	117.8 (5)

[a] Distances of iron from the centroids of the cyclopentadienyl (Cp) rings. Individual Fe···C distances vary from 2.00 to 2.11 Å for Fe1 and from 1.99 to 2.10 Å for Fe2, averaging 2.05 Å for Fe1···C and Fe2···C. Bond angles at the boron atom are between 102.7 and 112.7° with a mean value of 109.5°.

Attempts to replace the coordinated solvent molecule with a more donating solvent, e.g. acetonitrile, led to inconclusive results. In fact, addition of a few percent of CH_3CN to a CD_2Cl_2 solution of **1** results in an instantaneous color change from deep red to yellow and the corresponding ^{31}P NMR spectrum indicates the total disappearance of the initial doublet and its replacement by a number of resonances, some of which are attributable to η^1-bis(phosphine) and free phosphine.

A similar temperature dependence of the ^{31}P NMR spectrum is observed also for the iridium(I) derivative **4**. The single sharp resonance at δ 7.7 observed at room temperature in a saturated CD_2Cl_2 solution of $[Ir(dppf)_2]^+$ is converted into an AA′BB′ multiplet (Table I) and to a very broad singlet at ca. δ 8, when the solution is cooled at –90 °C. These data suggest the existence of a dimeric species $[Ir(dppf)(\mu\text{-dppf})]_2^{2+}$ (**7**) in equilibrium with a more labile species, likely a solvento complex analogous to that observed for the rhodium derivative.

X-ray Structure of $[Ir(dppf)_2]BPh_4$ (4). The crystal structure of **4** is shown in Figure 5. The compound contains cationic units in which the iridium atoms are four-coordinate with a geometric ligand configuration intermediate between square planar and tetrahedral.

The measure of the distortion from planarity can be well evaluated by the following structural features: (i) the coordination planes of the two ligands, defined by P1, P2, Ir and P3, P4, Ir,

Table IV. Fractional Atomic Coordinates (Esd's in Parentheses)

atom	*x/a*	*y/b*	*z/c*
Ir1	0.86646 (2)	0.49835 (7)	0.05852 (3)
Fe1	0.79873 (8)	0.34018 (22)	−0.04433 (12)
Fe2	0.95540 (7)	0.48616 (24)	0.16118 (11)
P1	0.8312 (1)	0.3844 (4)	0.0762 (2)
P2	0.8397 (1)	0.5344 (3)	−0.0219 (2)
P3	0.9192 (1)	0.5196 (4)	0.0380 (1)
P4	0.8776 (1)	0.5439 (4)	0.1426 (2)
B1	0.6247 (7)	0.4973 (22)	0.6535 (10)
C2	0.7771 (3)	0.4912 (9)	0.0869 (5)
C3	0.7472 (3)	0.5125 (9)	0.1037 (5)
C4	0.7318 (3)	0.4515 (9)	0.1334 (5)
C5	0.7462 (3)	0.3693 (9)	0.1464 (5)
C6	0.7760 (3)	0.3480 (9)	0.1297 (5)
C1	0.7915 (3)	0.4090 (9)	0.0999 (5)
C8	0.8459 (3)	0.3077 (8)	0.1728 (5)
C9	0.8608 (3)	0.2459 (8)	0.2066 (5)
C10	0.8795 (3)	0.1771 (8)	0.1888 (5)
C11	0.8834 (3)	0.1702 (8)	0.1372 (5)
C12	0.8686 (3)	0.2320 (8)	0.1034 (5)
C7	0.8498 (3)	0.3007 (8)	0.1212 (5)
C14	0.7929 (3)	0.2563 (10)	0.0160 (5)
C15	0.7949 (3)	0.2031 (10)	−0.0279 (5)
C16	0.8247 (3)	0.2222 (10)	−0.0479 (5)
C17	0.8410 (3)	0.2872 (10)	−0.0162 (5)
C13	0.8213 (3)	0.3082 (10)	0.0233 (5)
C19	0.7750 (3)	0.4584 (10)	−0.0390 (4)
C20	0.7573 (3)	0.4048 (10)	−0.0758 (4)
C21	0.7776 (3)	0.3848 (10)	−0.1147 (4)
C22	0.8078 (3)	0.4260 (10)	−0.1020 (4)
C18	0.8062 (3)	0.4715 (10)	−0.0552 (4)
C24	0.7937 (3)	0.6709 (10)	−0.0455 (5)
C25	0.7806 (3)	0.7561 (10)	−0.0396 (5)
C26	0.7924 (3)	0.8112 (10)	0.0001 (5)
C27	0.8173 (3)	0.7811 (10)	0.0341 (5)
C28	0.8304 (3)	0.6959 (10)	0.0282 (5)
C23	0.8186 (3)	0.6408 (10)	−0.0115 (5)
C30	0.8829 (3)	0.4925 (7)	−0.0934 (4)
C31	0.9000 (3)	0.5079 (7)	−0.1356 (4)
C32	0.8964 (3)	0.5888 (7)	−0.1619 (4)
C33	0.8755 (3)	0.6544 (7)	−0.1461 (4)
C34	0.8583 (3)	0.6390 (7)	−0.1040 (4)
C29	0.8620 (3)	0.5580 (7)	−0.0776 (4)
C36	0.9473 (3)	0.4157 (8)	−0.0376 (5)
C37	0.9547 (3)	0.3340 (8)	−0.0596 (5)
C38	0.9446 (3)	0.2535 (8)	−0.0390 (5)
C39	0.9272 (3)	0.2548 (8)	0.0036 (5)
C40	0.9198 (3)	0.3365 (8)	0.0256 (5)
C35	0.9299 (3)	0.4170 (8)	0.0050 (5)
C42	0.9652 (2)	0.6272 (8)	−0.0070 (5)
C43	0.9751 (2)	0.7051 (8)	−0.0304 (5)
C44	0.9528 (2)	0.7717 (8)	−0.0452 (5)
C45	0.9206 (2)	0.7605 (8)	−0.0365 (5)
C46	0.9107 (2)	0.6826 (8)	−0.0130 (5)
C41	0.9329 (2)	0.6159 (8)	0.0016 (5)
C48	0.9750 (3)	0.4426 (8)	0.0980 (5)
C49	1.0000 (3)	0.4703 (8)	0.1340 (5)
C50	0.9950 (3)	0.5623 (8)	0.1453 (5)
C51	0.9669 (3)	0.5914 (8)	0.1162 (5)
C47	0.9545 (3)	0.5174 (8)	0.0870 (5)
C53	0.9202 (3)	0.4000 (9)	0.1778 (5)
C54	0.9468 (3)	0.3858 (9)	0.2136 (5)
C55	0.9536 (3)	0.4680 (9)	0.2394 (5)
C56	0.9312 (3)	0.5331 (9)	0.2196 (5)
C52	0.9105 (3)	0.4910 (9)	0.1815 (5)
C58	0.8992 (3)	0.7126 (9)	0.1083 (4)
C59	0.9056 (3)	0.8042 (9)	0.1140 (4)
C60	0.8999 (3)	0.8475 (9)	0.1591 (4)
C61	0.8880 (3)	0.7993 (9)	0.1985 (4)
C62	0.8816 (3)	0.7077 (9)	0.1929 (4)
C57	0.8872 (3)	0.6643 (9)	0.1478 (4)
C64	0.8479 (3)	0.4928 (10)	0.2300 (5)
C65	0.8233 (3)	0.4957 (10)	0.2624 (5)
C66	0.7956 (3)	0.5457 (10)	0.2493 (5)
C67	0.7927 (3)	0.5929 (10)	0.2037 (5)
C68	0.8173 (3)	0.5901 (10)	0.1712 (5)
C63	0.8449 (3)	0.5400 (10)	0.1844 (5)
C70	0.5885 (3)	0.4934 (13)	0.5655 (5)
C71	0.5833 (3)	0.4988 (13)	0.5129 (5)
C72	0.6093 (3)	0.5057 (13)	0.4833 (5)
C73	0.6405 (3)	0.5074 (13)	0.5062 (5)
C74	0.6457 (3)	0.5020 (13)	0.5588 (5)
C69	0.6197 (3)	0.4951 (13)	0.5884 (5)
C76	0.5843 (4)	0.3700 (10)	0.6669 (5)
C77	0.5602 (4)	0.3282 (10)	0.6917 (5)
C78	0.5454 (4)	0.3739 (10)	0.7295 (5)
C79	0.5548 (4)	0.4614 (10)	0.7424 (5)
C80	0.5789 (4)	0.5032 (10)	0.7176 (5)
C75	0.5937 (4)	0.4575 (10)	0.6798 (5)
C82	0.6597 (3)	0.6436 (10)	0.6863 (6)
C83	0.6635 (3)	0.7361 (10)	0.6931 (6)
C84	0.6380 (3)	0.7940 (10)	0.6797 (6)
C85	0.6087 (3)	0.7595 (10)	0.6596 (6)
C86	0.6049 (3)	0.6670 (10)	0.6529 (6)
C81	0.6304 (3)	0.6091 (10)	0.6662 (6)
C88	0.6661 (4)	0.4453 (11)	0.7281 (6)

form a dihedral angle of 51° and angles of 24 and 27°, respectively, with the idealized mean plane defined by the four P atoms; (ii) the P atoms are severely displaced from the idealized mean plane (distances (Å) from the plane: P1, 0.79; P2, −0.61; P3, 0.70; P4, −0.83); (iii) the P–Ir–P angles involving nonadjacent P atoms are 140.6 and 145.9°, with a mean value of 143.3°, which is intermediate between the values for the square-planar and tetrahedral geometries.

This distortion from the usual planar geometry of Ir(I) complexes (the highest reported so far)[13] is evidently due to the steric requirements of the bulky dppf ligands in finding a mutually acceptable arrangement in a regular square-planar geometry. Analysis of molecular models clearly shows, in fact, that such geometry would lead to an unacceptable constraint of the phenyl groups of the bis(phosphine) ligand. On the other hand, the dppf molecule turns out to be a rather flexible chelating ligand, as shown by the chelation angle of 94° observed in **4**, which should be compared with those of 105° observed in $NiCl_2(dppf)$[5d] and 103.6° found in $[Pt_2(\mu\text{-}H)(\mu\text{-}CO)(dppf)_2]^{2+}$.[14] Moreover, the maintenance of a substantial parallelism between the cyclopentadienyl rings (7° (average) (Ir) vs 4.5° (Ni)) is made possible by fairly different M–P–C_5H_4 angles, i.e. 123.2° (mean) for Ir and 113.5° (mean) for Ni. Interestingly enough, although the four P atoms belong in pairs to independent ligands, they form a rather regular environment around the metal atom, the P···P contacts within a ligand being comparable to adjacent P···P contacts between the ligands (see Table III).

The two Cp···Cp lines passing through the centroids of the two pairs of cyclopentadienyl rings form an angle of 68°, showing that the four rings form an elongated distorted tetrahedron around the iridium atom, as confirmed by the angle of 69° between the planes defined by Cp1, Cp2, Ir and Cp3, Cp4, Ir. The Cp rings are staggered, being rotated by 35° (Cp1 with respect to Cp2) and by 25° (Cp3 with respect to Cp4), around the Cp···Cp axes. As already observed in other complexes of dppf, the two Cp planes are not exactly parallel, being inclined by 9.3° (Cp1 to Cp2) and 4.8° (Cp3 to Cp4), respectively.

The BPh_4^- anions do not chemically interact with the cationic unities, and the relevant structural details correspond to the expected values. In particular, the mean value (1.69 Å) of the four B–C distances corresponds exactly to the sum of the covalent radii.

Conclusions

The data here described confirm the recent report[6] on an unprecedented behavior of 1,1′-bis(diphenylphosphino)ferrocene as a ligand, i.e. a bidentate bridging ligating ability. We demonstrate this behavior in solution for tetracoordinated homoleptic, and

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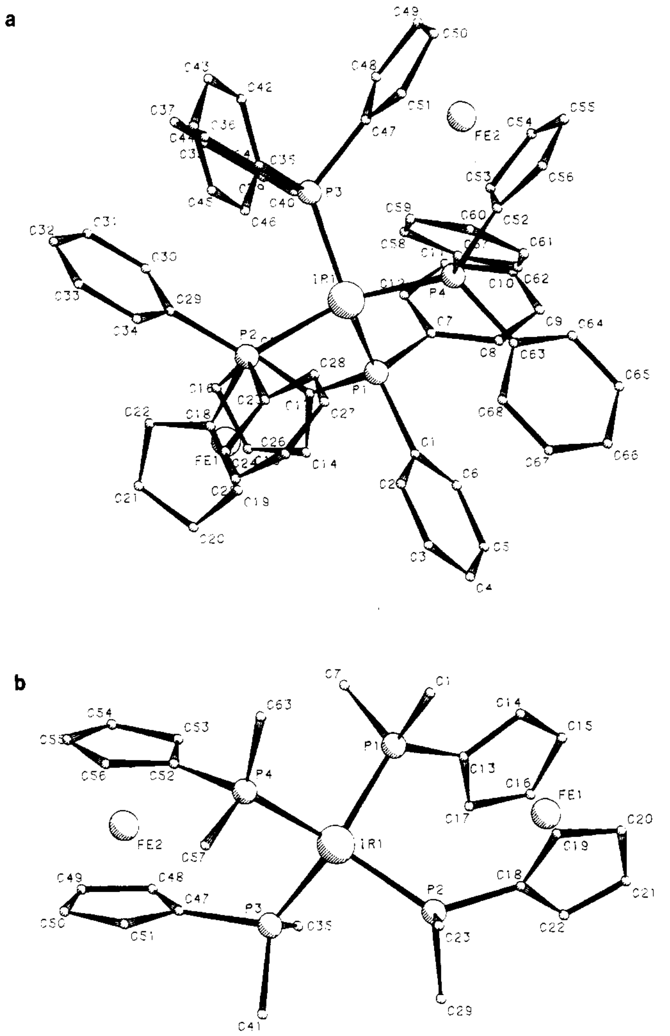

Figure 5. (a) Molecular structure of the cation complex $[Ir(dppf)_2]^+$ of **4** showing the numbering scheme. (b) View of the same cation with only the first atom in each phenyl ring.

expectedly very crowded, complexes, which can exist thanks to the exceptional geometric flexibility of dppf. In fact, molecular models clearly show that the bridging bonding ability of dppf in complexes **5** and **7** is made possible by the easy mutual rotation of the two $C_5H_4PPh_2$ rings. Apparently this coordination mode is preferred in solution thanks to probably significant solvation effects. In the absence of such thermodynamic contribution, $[Ir(dppf)_2]^+$ and, tentatively, $[Rh(dppf)_2]^+$ are obtained as "conventional" monomeric complex cations, as observed[12] for $[RhL_2]^+$ in which L is $Ph_2P(CH_2)_nPPh_2$ and $n = 2-4$. In conclusion, the major difference between the ligating behaviors toward Rh(I) of dppe and dppp, on the one side, and dppf on the other side, appears to be in the relative stability of the dinuclear species, which is evidently greater for dppf.

Experimental Section

General Procedures and Materials. Syntheses and manipulations of solutions were performed under a nitrogen atmosphere with standard Schlenk-line techniques. All solvents were dried by standard procedures. ^1H and ^{31}P NMR spectra were recorded on a JEOL 90 Q spectrometer equipped with a variable-temperature apparatus and were referenced to internal $SiMe_4$ and external H_3PO_4 (85% w/w), respectively. The ^{31}P NMR spectra were simulated by using the computer program PANIC provided by Bruker Instrument Co. The final parameters gave a fit to the observed line position better than 0.5 Hz. IR spectra were recorded on a Perkin-Elmer 599 B spectrometer. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) was from Strem Chemicals and was used as received. The dinuclear complexes $[RhCl(COD)]_2$,[15] $[IrCl(COD)]_2$,[16] and $[IrCl(COT)_2]_2$[16] (COD = 1,5-cyclooctadiene; COT = cyclooctene) were synthesized according to literature methods.

$[Rh(dppf)_2]B(C_6H_5)_4$ (1). A solution of $[RhCl(COD)]_2$ (0.500 g, 1.014 mmol) in 1,2-dichloroethane (15 mL) and dppf (2.249 g, 4.056 mmol) was heated to reflux for 2 h. The volatiles were vacuum-evaporated and the residue dissolved in 5 mL of DCE. Addition of $NaBPh_4$ (694 mg, 2.028 mmol) in methanol (30 mL) formed a brick-red precipitate that dissolved upon heating at reflux temperature. After a few hours a yellow solid was precipitated, which was recovered by filtration and dried under vacuum. Dissolution of the crude product in CH_2Cl_2 (50 mL) gave a red solution, and reprecipitation with ethanol (70 mL) at room temperature originated a red precipitate (*red form* of **1**). After the suspension was heated at reflux temperature for ca. 1 h, the yellow precipitate separated out. The yield of pure **1** (*yellow form*) was 2.64 g (87%). Anal. Calcd for $C_{92}H_{76}Fe_2P_4BRh$: C, 72.18; H, 5.00. Found: C, 71.99; H, 4.93. ^1H NMR in CD_2Cl_2 at 27 °C: δ 8.0–6.8 (complex multiplet, 60 H, C_6H_5), 4.13 (apparent triplet with $J = 1.8$ Hz, 8 H, C_5H_4), 3.71 (unresolved triplet, 8 H, C_5H_4). When the recrystallization of the crude product was carried out in DCE/CH_3OH, the red form of **1** contained 1,2-dichloroethane of crystallization, as determined by ^1H NMR spectroscopy and confirmed by elemental analysis. Anal. Calcd for $C_{95.3}H_{82.6}BFe_2Cl_{3.3}P_4Rh$: C, 67.56; H, 4.91; Cl, 6.90. Found: C, 67.44; H, 4.95; Cl, 6.95. The yellow form obtained by heating at reflux temperature a suspension of **1** in DCE/CH_3OH contained a smaller amount of crystallization solvent. Anal. Calcd for $C_{93.3}H_{78.6}BFe_2Cl_{1.3}P_4Rh$: C, 70.25; H, 4.96; Cl, 2.89. Found: C, 70.51; H, 4.99; Cl, 3.02.

$[Ir(dppf)_2]ClO_4$ (2). *Safety Note.* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

To a stirred suspension of $[IrCl(cyclooctene)_2]_2$ (500 mg, 0.558 mmol) and dppf (1.237 g, 2.23 mmol) in 20 mL of acetone was added a solution of $TlClO_4$ (339 mg, 1.116 mmol) in acetone (20 mL). The reaction mixture was stirred at room temperature for 18 h, and then the volatiles were evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (30 mL), and the solution was filtered to eliminate TlCl. The filtrate was concentrated to 5 mL under vacuum, and acetone (40 mL) was added. In a few hours a yellow precipitate was formed. The yield of the solid, recovered by filtration, washed with acetone, and dried under vacuum, was 1.01 g (65%). Anal. Calcd for $C_{68}H_{56}Fe_2P_4O_4ClIr$: C, 58.32; H, 4.03. Found: C, 57.55; H, 4.22.

$[Ir(dppf)_2]BPh_4$ (4). A water solution of $NaBPh_4$ was added to a solution of **2** (500 mg) in CH_2Cl_2 (20 mL). The mixture was stirred for 30 min, and the orange layer separated out. The treatment with $NaBPh_4$ was repeated three times. The organic solution was washed two times with 20 mL of H_2O and then vacuum-evaporated. Addition of CH_3OH to the residue dissolved in CH_2Cl_2 (10 mL) afforded a red precipitate. The solid was purified by recrystallization from dichloromethane/*n*-hexane to give 510 mg of pure, microcrystalline **4** (yield 87%). Calcd for $C_{92}H_{76}P_4Fe_2BIr$: C, 68.20; H, 4.73. Found: C, 68.10; H, 4.82.

$[Ir(dppf)(H)(Cl)]_2(\mu\text{-dppf}(-2H))$ (3). A solution of $[Ir(COD)Cl]_2$ (410 mg, 0.611 mmol) and dppf (1.367 g, 2.466 mmol) in toluene (20 mL) was heated at reflux temperature for 6 h. A yellow-beige precipitate was formed, which was recovered by filtration, washed with *n*-hexane, and dried under vacuum. The yield of pure **3** was 0.20 g (15%). Anal. Calcd for $C_{102}H_{84}P_6Fe_3Ir_2Cl_2$: C, 57.83; H, 4.00. Found: C, 57.37; H, 3.86. After the filtrate was concentrated under vacuum, additional product was obtained (0.63 g), which, however, was contaminated by free dppf.

X-ray Structure of $[Ir(dppf)_2]BPh_4$. Suitable crystals were obtained by slow evaporation of a CH_2Cl_2/C_2H_5OH solution of **4**. A small crystal fragment, of maximum dimension 0.2 mm, was used for intensity data collection on a Philips four-circle computer-controlled diffractometer with a graphite monochromator. Crystal and intensity data are given in Table II. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares analysis to the final *R* of 8.4%, when the largest shift on the parameters refined was $<0.1\sigma$. The function minimized was $\sum w(\Delta F)^2$ with $w = 1$. The ring carbon atoms were refined as rigid bodies with H atoms introduced in calculated positions. Anisotropy was introduced only for the non-carbon atoms. The final Fourier difference map showed some residuals of electronic density, which were interpreted as due to possible presence of a disordered solvent molecule. However, because of the distribution of the residuals over a large number of positions, it was impossible to rationalize a correct model for this molecule, and no coordinates are given for these atoms. The

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presence of a trace amount of C_2H_5OH was confirmed by ^1H NMR spectroscopy (in an estimated molar ratio ethanol/complex of ca. 0.2). Calculations were done by using the SHELX program system.[17] Final atomic coordinates are listed in Table IV; bond lengths and bond angles are reported in Table III.

Acknowledgment. We are grateful to Professor G. M. Bonora for recording the ^{31}P NMR spectra at 162 MHz and to Professor A. Gambaro for the ^{31}P NMR spectral simulation.

Supplementary Material Available: A table of thermal parameters (2 pages); a list of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Products and Kinetics of the Direct, Specific Transmetalation of $(\mu_4\text{-O})N_4Cu(Ni(H_2O))_3Cl_6$ (N = *N,N*-Diethylnicotinamide) by $M(NS)_n$ Reagents (NS = Monoanionic *S*-Methyl Isopropylidenehydrazinecarbodithioate) in Nitrobenzene: A Relationship between Precursor Stabilities and Product Formation Rates

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Received October 5, 1989

The first kinetic study of specific, stoichiometric monotransmetalations of a heteropolymetallic molecule is reported. The copper(II) center of the target $(\mu_4\text{-O})N_4Cu(Ni(H_2O))_3Cl_6$ (D) is specifically replaced by cobalt or zinc from transmetalators $Co(NS)_2$ (B_1), $Zn(NS)_2$ (B_3), and $Co(NS)_3$ (E). Here, N is *N,N*-diethylnicotinamide and NS is monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate. The rate laws for monotransmetalations of $(\mu_4\text{-O})N_4Cu_4Cl_6$ (A) by B_1, $Ni(NS)_2$ (B_2), and B_3 are third-order in nitrobenzene. Although the reaction of D with B_2 is also third-order, those with B_1 and B_3 are of the form rate = $k_4\beta_1[D][B_1 \text{ or } B_3]/(1 + \beta_1[D])$, where k_4 is the first-order rate constant for conversion of 1:1 reaction precursors (with equilibrium constants β_1) to products. Two precursors of stoichiometry D·B_3 exist at different temperatures in nitrobenzene. More stable transmetalation precursors are converted to products at lower rates. The structural–mechanistic origins of monotransmetalation specificity in these systems are discussed.

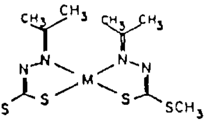
Introduction

There is a great deal of current interest in the structures and reactivities of heteropolymetallic complexes and clusters.[1] Our contribution to this area is to develop transmetalation, which is defined[2] as the stoichiometric replacement of metals in a polymetallic target with different metals from reagents called transmetalators. Transmetalation is a rich source of many new heteropolymetallic molecules.[2] *Direct* transmetalation reactions leave the target molecularity unchanged. *Monotransmetalation* refers to the replacement of just one of several metal centers in a target. The replacement of a particular element in a heteropolymetallic target is said to be *specific*.[2]

Equation 1, an example of direct[2-4] copper(II) transmetalation reactions, can be used to generate large families of new molecules containing up to four different metals.[4] Here, N is monodentate

$$\underset{\text{A}}{(\mu_4\text{-O})N_4Cu_4X_6} + x\underset{\text{B or C}}{M(NS)_2} \rightarrow (\mu_4\text{-O})N_4Cu_{4-x}M_xX_6 + x\underset{\text{B or C}}{Cu(NS)_2} \quad (1)$$

N,N-diethylnicotinamide, X is Cl or Br, x = 1–4, M is Co,[4] Ni,[3] or Zn,[4] and NS is a monoanionic *S*-methyl hydrazinecarbodithioate ligand in complexes B and C. The driving force of eqs 1 is the formation of especially stable coproduct $Cu(NS)_2$.[2-4]



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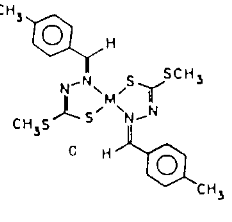

C

Transmetalation reactions 1 proceed stoichiometrically under mild conditions, and the products are easily separated.[2-4] Kinetic measurements in systems of known structure (A,[2] B;[5-7] Figure 1) help to identify the basic structural requirements for efficient metal exchange.[8-11]

We have measured the rates of copper(II) monotransmetalation in A by B and C (M = Co, Ni, Zn and x = 1 in eq 1) in aprotic solvents. We found different rate laws 2–4, where TM is a

$$\text{rate} = k_2[\text{TM}][\text{A}]^2 \quad (2)$$

$$\text{rate} = k_3[\text{TM}][\text{A}] \quad (3)$$

$$\text{rate} = k_4[\text{TM}] \quad (4)$$

$$\text{TM} + n\text{A} \rightleftarrows \text{TM}\cdot\text{A}_n \quad \beta_n \quad (5)$$

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