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1,1′-Bis(diphenylphosphino)ferrocene Complexes of Platinum(II) and Platinum(I). Crystal and Molecular Structure of $[(L\text{-}L)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(L\text{-}L)][BF_4]\cdot0.5H_2O$, Where L-L = $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$

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A series of platinum(II) derivatives with 1,1′-bis(diphenylphosphino)ferrocene (L-L) were synthesized and characterized in solution mainly by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The series includes, besides the known $Pt(L\text{-}L)Cl_2$ (**1**), the mononuclear species $Pt(L\text{-}L)(pz)_2$ (**2**, pzH = pyrazole), $Pt(L\text{-}L)(3,5\text{-}Me_2pz)$ (**3**, $3,5\text{-}Me_2pzH$ = 3,5-dimethylpyrazole), $[Pt(L\text{-}L)(3,5\text{-}Me_2pzH)_2][BF_4]_2$ (**4**), and $[Pt(L\text{-}L)(H_2O)_2][BF_4]_2\cdot xH_2O$ (**5**) as well as the dinuclear species $[(L\text{-}L)Pt(\mu\text{-}OH)_2Pt(L\text{-}L)][BF_4]_2$ (**6**) and $[Pt_2(L\text{-}L)_2H_3][BF_4]$ (**7**). Reaction of the hydrido complex **7** with CO (room temperature, 1 atm) gave $[(L\text{-}L)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(L\text{-}L)][BF_4]$ (**8**), formally a platinum(I) derivative. The molecular structure of $[(L\text{-}L)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(L\text{-}L)][BF_4]\cdot0.5H_2O$ (**8a**) was determined by X-ray analysis: the complex crystallizes in the triclinic space group $P\bar{1}$ with a = 12.411 (4) Å, b = 15.930 (5) Å, c = 16.922 (7) Å, α = 100.64 (3)°, β = 98.74 (3)°, γ = 104.34 (3)°, Z = 2, and V = 3166 (4) Å^3. The structure was refined to a conventional R factor of 0.025. In the dinuclear cation, the platinum atoms have cis-square-planar coordination, which shows a significant distortion toward tetrahedral geometry with P–Pt–P angles of 103.68 (6) and 103.64 (6)°. The Pt–Pt distance is 2.790 Å.

Introduction

The synthesis and reactivity of transition-metal complexes with ferrocene-bridged bis(tertiary phosphine) ligands such as 1,1′-bis(diphenylphosphino)ferrocene (L-L) has been a topic of interest in the last few years owing mainly to the catalytic properties displayed by some of them.[1-5] Thus, complexes such as $Pd(L\text{-}L)Cl_2$ have achieved great success in synthetic organic chemistry as catalysts in a variety of cross-coupling reactions[6] whereas cationic rhodium(I) complexes are known to be efficient hydrogenation catalysts for olefins.[7] More recently, complexes with chiral ferrocenylphosphines have been shown to be relevant in asymmetric synthesis: rhodium(I)[8,9] and platinum(II)[10] derivatives have been reported as hydrogenation and hydrosilylation catalysts, respectively. Gold(I) species have been found to be catalysts in aldol reactions of enolates with aldehydes to give optically active β-hydroxycarbonyl compounds.[11]

Complexes of these ligands are of interest even from a purely structural viewpoint: indeed, recent X-ray work has underlined some peculiar features of these molecules, related mainly to the bulkiness of the ligands, and opened several questions, e.g. the influence of the possible conformations of the cyclopentadienyl rings (eclipsed or staggered) on the catalytic properties of the system.

In the last several years we have synthesized several series of platinum complexes with chelating bis(phosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$, and investigated aspects of their reactivity:[12] in a few cases, the structures in the solid state were determined by diffractometric methods.

On account of the present interest in the chemistry of transition-metal derivatives with diphosphines containing the ferrocene moiety, we have now extended our investigations to complexes of 1,1′-bis(diphenylphosphino)ferrocene: here we report the synthesis and characterization of several platinum(II) derivatives, including a dinuclear trihydrido species, $[Pt_2(L\text{-}L)_2H_3][BF_4]$, and of one formally platinum(I) species. The crystal and molecular structure of the last compound, $[(L\text{-}L)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(L\text{-}L)][BF_4]\cdot0.5H_2O$, was determined by X-ray analysis. A comparison with the structure of the complex having L-L = $Ph_2P(CH_2)_2PPh_2$, previously described, is made.[12e]

A preliminary report of this work has been given.[13]

Results and Discussion

The syntheses of the complexes **1–8** are summarized in Scheme I. The starting derivative, $Pt(L\text{-}L)Cl_2$ (**1**), was obtained either from $K_2[PtCl_4]$, $(CH_3)_2S$, and L-L according to the method of Whitesides and co-workers[1] or by reaction of L-L with $Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene) in chloroform solution. The latter was found previously to be an intermediate from which several other $Pt(P\text{-}P)Cl_2$ derivatives (P-P = bis(tertiary phosphines)) were obtained in good yields.[12]

The complex **1** was characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR.

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Scheme I

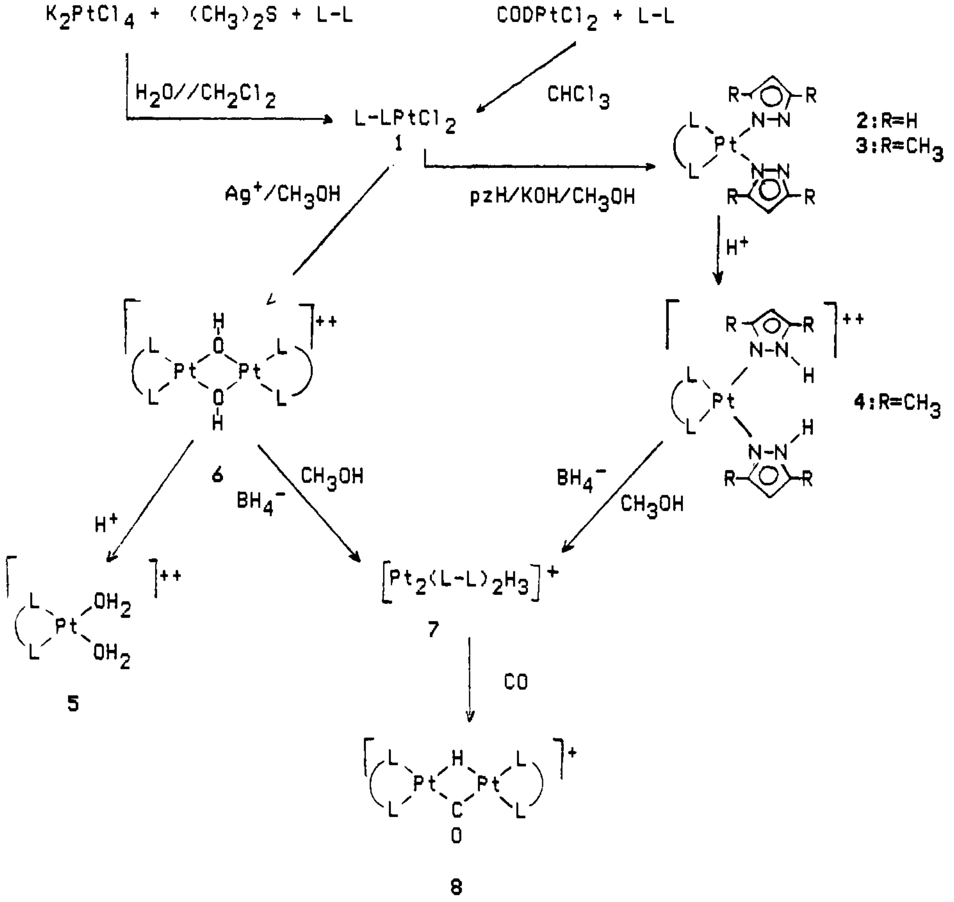

Table I ^1H and $^{31}P\{^1H\}$ NMR Spectral Data[a]

	^1H									$^{31}P\{^1H\}$	
		Cp				pz					
compd	Ar[b]	β	α	J_{HH}	J_{PH}	3	4	5	others		$^1J_{PtP}$
ligand	7.4–7.2	4.32 m	4.07 m	1.95	2.34					−17.2	
1	8.0–7.7, 7.5–7.2	4.37 m	4.19 m	2.05	2.17					12.94	3765
2	7.9–7.6, 7.5–7.1	4.35 s				7.0 br	5.67 br	6.70 d[c]		7.20	3198
3	7.8–7.0	4.41 s br, 4.33 s br				1.76 s	5.12 s[d]	1.71 s		5.46	3166
4	8.6–8.3, 8.1–7.7, 7.5–7	5.13, 4.56, 4.36, 4.05				2.02 s	5.61 br	1.91 s	11.0 br[e]	−0.11	3500
5[f]										18.4	3973
6[g]	8.2–6.6	4.45, 4.27		1.5					−0.14[e]	9.4	3855
7[g,h]	7.7–7.2	4.31 br, 4.11 br							−4.7 qq	29.2	3280
8[g,i]	8.0–6.8	4.32 br, 4.07 br							−2.0 qq	25.5	3923

[a] Chemical shifts are in ppm (δ) downfield from Me_4Si(^1H) and 85% H_3PO_4 (^{31}P); coupling constants (J) are in Hz; spectra are of $CDCl_3$ solutions at room temperature unless otherwise stated. [b] Always a multiplet. [c] $J_{HH} = 1.8$ and $^3J_{PtH} = 10$. [d] $^4J_{PtH} = 10$. [e] Disappears with D_2O. [f] In 1,1,2,2-tetrachloroethane-d_2. [g] In dichloromethane-d_2. [h] Hydrido region, quintet of quintets, $^1J_{PtH} = 443$ and $^2J_{PH} = 40$, $^3J_{PtP} = 212$, $J_{PP} = 11$. [i] Hydrido region: room temperature, quintet of quintets, $^1J_{PtH} = 457$, $^2J_{PH} = 33.4$; at 203 K in deuterioacetone δ −1.57, quintet of triplets of triplets, $^1J_{PtH} = 453$, $^2J_{cis\text{-}PH} = 16.4$, and $^2J_{trans\text{-}PH} = 82$. $^{31}P\{^1H\}$ NMR (dichloromethane): room temperature, $^3J_{PtP} = 187$, $J_{PP} = 35$; 223 K, +31.0 ppm ($^1J_{PtP} = 4927$, $^3J_{PtP} = 600$, J_{PP} unresolved), +16.7 ppm ($^1J_{PtP} = 2892$, $^3J_{PtP}$ and J_{PP} unresolved).

The ^1H spectrum shows two complex multiplets at δ 4.37 and 4.19 ($CDCl_3$, room temperature): the overall pattern is quite similar to that of the free ligand.

In the attempt to assign the observed resonances to the protons of the cyclopentadienyl rings, the spectra of both the ligand and complex **1** were further analyzed by homonuclear ^1H 2D experiments at room temperature.

The COSY-90 spectra of the ligand and of complex **1** indicate the mutual coupling of the two resonances. The homonuclear J-resolved spectra (Figure 1) allow assignment to the α- and β-protons to be made. In the spectra of the ligand and complex **1**, H-H couplings are observed (1.95 Hz, ligand; 2.05 Hz, complex **1**) for the resonances at δ 4.32 and 4.37, respectively, whereas for the resonances at high field, δ 4.07 and 4.19, in addition, a coupling to the phosphorus atom (2.34 Hz, ligand; 2.17 Hz, complex **1**) is resolved.

In the $^{31}P\{^1H\}$ spectrum of complex **1**, one signal at 12.94 ppm (external reference 85% H_3PO_4) is observed, flanked by ^{195}Pt satellites with intensity ratio ca. 1/4/1, typical of a mononuclear species. The ^{31}P nucleus appears to be strongly deshielded with respect to that of the free ligand (−17.2 ppm). The $^1J_{PtP}$ value of 3765 Hz is at the upper end of the range expected for a phosphine trans to a chlorine (a ligand having a moderate trans influence). This suggests a rather long Pt^{II}–Cl bond (cf. $Pt[Ph_2P(CH_2)_nPPh_2]Cl_2$: $n = 2$, $^1J = 3618$ Hz; $n = 3$, $^1J = 3420$ Hz; $n = 4$, $^1J = 3662$ Hz).[14]

The structure of complex **1** has been reported:[15] the cyclo-

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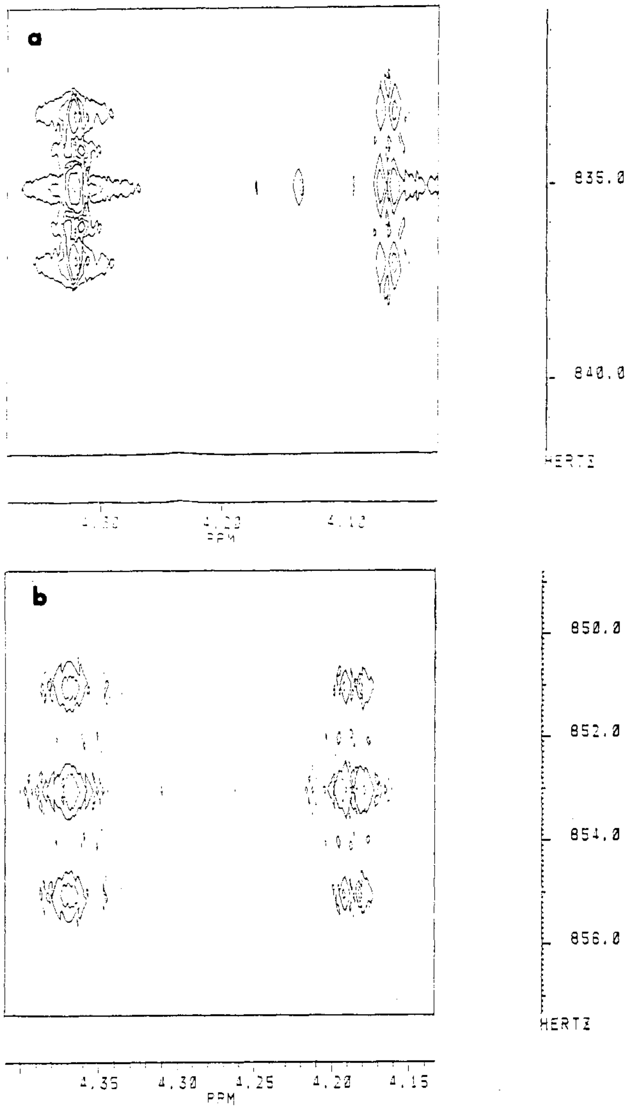

Figure 1. ^{1}H 2D NMR homonuclear *J*-resolved spectra of (a) the ligand 1,1′-bis(diphenylphosphino)ferrocene and (b) compound **1**.

pentadienyl rings were found to be in a staggered configuration.

The molecule displays the same peculiar feature observed previously in the palladium(II) homologue, i.e. a very large P–Pt–P angle of 99.3 (1)° (Pd(L-L)Cl$_2$·CH$_2$Cl$_2$, 97.98 (4)°;[16] Pd(L-L)Cl$_2$·CHCl$_3$, 99.07 (5)°).[6c] The large value of this angle, which implies a distortion of the square-planar geometry around the metal atom, is related to the unusual bite of the chelating ligand imposed by the ferrocenyl moiety bridging the two phosphorus atoms.

Reaction of **1** with pyrazole and 3,5-dimethylpyrazole in methanolic potassium hydroxide (molar ratio Pt/pzH/KOH = 1/2/2) afforded complexes **2** and **3**, respectively.

For **2** and **3** analytical and conductivity data and molecular weight determinations support a mononuclear species having a P$_2$N$_2$ arrangement around the platinum atom. The ^{1}H spectra of **2** and **3** show the equivalence, on the NMR time scale, of the two pyrazolato ligands: indeed, in both spectra, one set alone is observed for the protons of the heterocyclic ligand. In the spectrum of **2**, three signals, a broad pseudotriplet, one sharp doublet, and a broad unresolved signal, can be assigned to the 4, 5, and 3 protons, respectively. The doublet at δ 6.70 ($^3J_{HH}$ = 1.8 Hz) is assignable to the hydrogen nearer to the platinum atom, owing to the presence of satellites ($^3J_{PtH} \approx 10$ Hz). Actually a COSY-90 spectrum has evidenced that all three resonances are mutually coupled (Figure 2). A coupling of ca. 0.7 Hz between the 3- and 5-protons of a pyrazole ring has been observed recently in the spectra of some palladium complexes.[17]

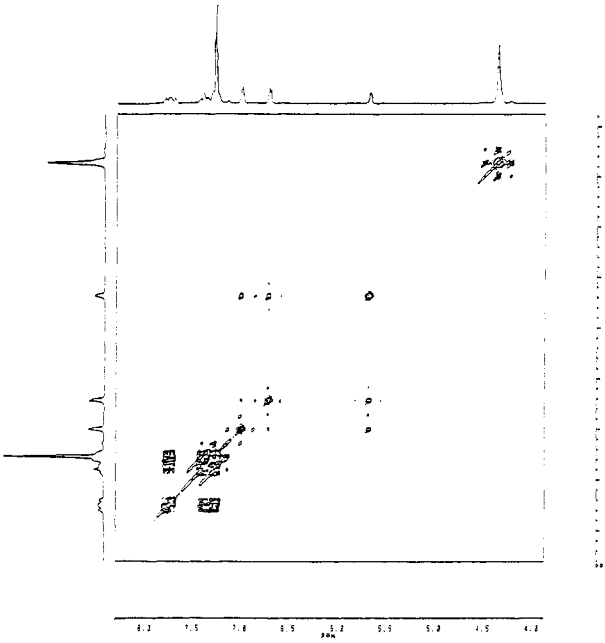

Figure 2. ^{1}H 2D NMR COSY-90 spectrum of compound **2**.

In the spectrum of **3**, two signals for the CH$_3$ substituents prove the complex to be nonfluxional even at room temperature: in this case the coupling to the ^{195}Pt nucleus was not resolved so that assignment to one or the other CH$_3$ group was thwarted.

In both complexes **2** and **3** the protons of the cyclopentadienyl rings give rise to a deceptively simple system, consisting of a sharp singlet at δ 4.35 for **2** and two signals at δ 4.41 and 4.33 for **3**. In both cases the intensity of the signals is in the correct ratio to that of the other protons.

The ^{31}P{^{1}H} spectra show one resonance at 7.2 ppm for **2** and at 5.46 ppm for **3**: the $^1J_{PtP}$ values 3198 (**2**) and 3166 Hz (**3**) are in agreement with a phosphorus trans to an anionic nitrogen ligand.

Protonation of **3** with acids having noncoordinating anions, such as HBF$_4$, afforded **4**. Analytical and other data fit a mononuclear species, [Pt(L-L)(3,5-Me$_2$pzH)$_2$][BF$_4$]$_2$. The observation in the ^{1}H NMR spectrum of a signal at low field (δ ca. 11.0, broad) that exchanges with D$_2$O proves that protonation takes place on the nitrogen atom not involved in the coordination to the metal. Once again two ^{1}H resonances are found for the methyl groups and one signal in the ^{31}P{^{1}H} spectrum (–0.11 ppm, CDCl$_3$, room temperature; $^1J_{PtP}$ = 3500 Hz).

Thus, it seems that in spite of the steric requirements of the bulky diphosphine, no cleavage of a platinum–nitrogen bond occurs on protonation of **3**.

The obtainment of complex **4** is remarkable since, as previously observed by us,[12d] the coordinated neutral pyrazole has a good leaving ability, thus making **4** a useful intermediate (see later).

Thus far only mononuclear species have been described; in contrast, treatment of the dichloride **1** with 2 equiv of AgBF$_4$ in methanol solution afforded the species [Pt(L-L)(OH)]$_n$[BF$_4$]$_n$, which is likely to be dimeric (n = 2, **6**), even if the available data do not allow us to rule out formulations where $n > 2$ with certainty.

Besides the IR spectra, which give evidence of an OH stretch (Nujol mull, ν(OH) ca. 3550 cm^{-1} (m)), support for the presence of an OH group comes from the ^{1}H spectra. Indeed, no resonances assignable to OCH$_3$ protons are observed, whereas a resonance at very high field (δ –0.14, broad), which disappears on exchange with D$_2$O, is likely to be due to a bridging hydroxo group.

No satellites with ^{195}Pt nuclei are observed, thus ruling out the possibility of a bridging hydride in place of an OH group. The lack of any observable coupling between platinum and the hy-

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drogen of a hydroxy group is not unprecedented.[18]

The $^{31}P\{^1H\}$ NMR spectrum gives evidence of a highly symmetric system, resulting in one resonance at 9.40 ppm. The $^1J_{PtP}$ coupling constant is very large, 3855 Hz, as expected for a phosphorus trans to a ligand having a low trans influence.

Protonation of **6** with aqueous HBF_4 in CH_2Cl_2 solution gives a mixture containing, according to $^{31}P\{^1H\}$ NMR, complex **6** and several other species. The same reaction, from a workup of the concentrated solution (see Experimental Section) affords a product which is analyzed as $[Pt(L\text{-}L)(H_2O)_2][BF_4]_2{\cdot}xH_2O$, $x = 0\text{–}1$. The compound is very unstable: thus, in CH_2Cl_2 solution the $^{31}P\{^1H\}$ NMR spectrum shows the existence of more species, including the hydroxo derivative **6**. If the $^{31}P\{^1H\}$ spectrum is carried out in *sym*-$C_2D_2Cl_4$ on a freshly dissolved sample, a main resonance at 18.4 ppm (singlet with satellites) is observed. When the solution stands, once again, other resonances appear, suggesting the existence of an equilibrium.

The value of $^1J_{PtP}$ (3973 Hz) related to the signal at 18.4 ppm assignable to the $[Pt(L\text{-}L)(H_2O)_2]^{2+}$ cation is consistent with the hypothesis of a phosphorus atom trans to a water molecule.

Additional molecules of water are likely to be hydrogen-bonded, in the solid state, to the tetrafluoroborate anions.

Reaction of both the mononuclear complex **4** and the dinuclear species **6** with KBH_4 (Pt/BH_4 molar ratio 1/1 for **4** and 2/1 for **6**) in methanol solution afforded a hydrido binuclear complex, $[Pt_2(L\text{-}L)_2H_3][BF_4]$ (**7**), similar to other platinum hydrides with chelating diphosphines. The structures of two analogous species $[Pt_2(P\text{-}P)_2H_3][X]$ (P-P = $(Ph_2PCH_2)_2$, X = BF_4;[12d,19] P-P = $[(t\text{-}Bu)_2P]_2(CH_2)_3$, X = BPh_4[20]) have been shown to differ in the solid state.

In the IR spectra of the new complex, **7** (Nujol and $CHCl_3$ solution), a medium and broad absorption centered at 2020 cm^{-1} ensures the presence of at least one terminal Pt–H bond. On the NMR time scale, the species is fluxional down to ca. −70 °C. The ^1H spectrum in the hydrido region displays a complex pattern of quintets (ca. 1:8:18:8:1) of quintets (δ −4.7): the first, nonbinomial, quintet arises from the superposition of the subspectra related to the three Pt–Pt, $^{195}Pt\text{–}Pt$, $^{195}Pt\text{–}^{195}Pt$ isotopomers and the other one from the coupling to four equivalent phosphorus atoms. The overall pattern of the hydrido resonance is well resolved and establishes the binuclear nature of complex **7**, suggesting a system having, on the NMR time scale, only bridging hydrides. The observed value of $^1J_{PtH}$, 443 Hz, is in agreement with the hydride ligands residing between the platinum nuclei; the $^2J_{PH}$ value, 40 Hz, as reported for similar species, is intermediate between the values observed for *trans*- and *cis*-H_2PtP_2 square-planar complexes.[12d] The $^{31}P\{^1H\}$ spectrum shows, as expected, one resonance at 29.25 ppm ($^1J_{PtP}$ = 3280 Hz, $^3J_{PtP}$ = 212 Hz, and J_{PP} = 11 Hz), in agreement with the equivalence of the phosphorus nuclei.

In the absence of X-ray data no speculation is possible on the structure of the complex in the solid state.

When CO (room temperature) is bubbled in an acetone solution of complex **7**, a deep orange color develops: from the solution, complex **8**, $[(L\text{-}L)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(L\text{-}L)][BF_4]$, can be isolated by addition of diethyl ether.

In the IR spectrum, no absorptions are observed around 2000 cm^{-1}, suggesting no terminal bonding for the hydrogen atom and for the carbonyl group. A strong band at 1770 cm^{-1} is assigned to a bridging carbonyl: the wavenumber, although not unprecedented,[12e] is somewhat lower than expected in a cationic complex. The presence of a bridging hydride was ascertained through the ^1H NMR spectrum: at room temperature ($CDCl_3$ solution) a quintet of quintets, centered at δ −2.0, was observed, as in the parent trihydrido complex **7**, suggesting a dynamic process. When the temperature is lowered, fluxionality gradually disappears and at ca. −70 °C (CD_3COCD_3) the spectrum consists of a quintet ($^1J_{PtH}$ = 453 Hz) of triplets of triplets ($^2J_{PH}$ = 82 and 16.4 Hz, respectively). The $^{31}P\{^1H\}$ spectrum at 35 °C (CD_2Cl_2) consists of a single signal at 25.5 ppm ($^1J_{PtP}$ = 3923 Hz, $^3J_{PtP}$ = 187 Hz, J_{PP} = 35 Hz): at low temperature (−50 °C) the ^{31}P resonance is split into two signals at 31.0 and 16.7 ppm with $^1J_{PtP}$ = 4927 and 2892 Hz, respectively.

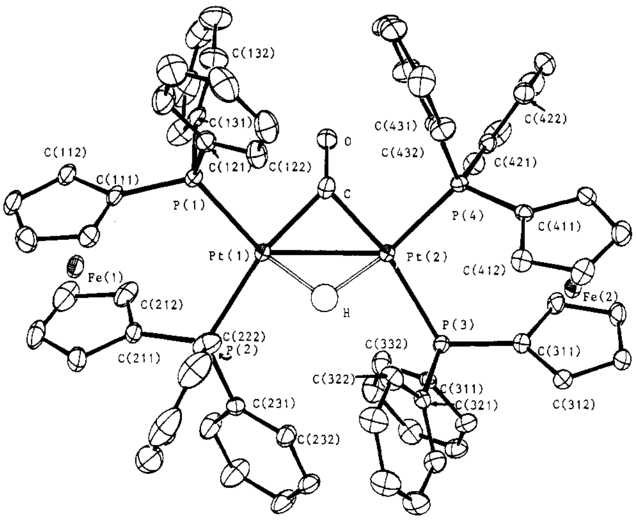

Figure 3. ORTEP drawing of **8a**. Thermal ellipsoids are drawn at 30% probability.

Table II. Crystallographic Data for $[Pt_2(\mu\text{-}H)(\mu\text{-}CO)(L\text{-}L)_2]BF_4{\cdot}0.5H_2O$

formula	$C_{69}H_{57}BF_4Fe_2OP_4Pt_2{\cdot}0.5H_2O$	V, Å^3	3166 (4)
fw	1623.81	Z	2
space group	$P\bar{1}$	D_{calcd}, g cm^{-3}	1.730
a, Å	12.411 (4)	μ(Mo Kα), cm^{-1}	51.35
b, Å	15.930 (5)	min transmission factor	0.71
c, Å	16.922 (7)	final R and R_w indices[a]	0.025, 0.029
α, deg	100.64 (3)		
β, deg	98.74 (3)		
γ, deg	104.34 (3)		

[a] $R = \sum(F_o - k|F_c|)/\sum F_o$. $R_w = [\sum w(F_o - k|F_o|)^2/\sum wF_o^2]^{1/2}$.

All the evidence obtained by the NMR spectra at low temperature are in agreement with a complex having both hydrido and CO ligands bridging the two platinum atoms, trans to two phosphorus nuclei and cis to the other two. The resonance at 31.0 ppm is assigned to the phosphorus trans to the hydrido ligand: the low trans influence of a bridging hydride has been observed previously.[21] Such an arrangement was confirmed, in the solid state, by the resolution of the structure of the complex $[(L\text{-}L)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(L\text{-}L)][BF_4]{\cdot}0.5H_2O$ (**8a**) by X-ray analysis.

Structure in the Solid State of Complex 8a. Crystals of compound **8a** are triclinic and centrosymmetric, and the unit cell contains two $[Pt_2(\mu\text{-}H)(\mu\text{-}CO)(L\text{-}L)_2]^+$ cations, two BF_4^- anions, and one disordered water molecule, lying on a space group general position with occupancy factor of ca. 0.5. The water molecule is linked to the BF_4^- anion via a weak hydrogen bond (shortest F···OW contact 3.013 (8) Å). The closest non-hydrogen atom contact between the cation and the anion is 3.144 (8) Å (C(422)···F(2) interaction).

An ORTEP view of the cation of **8a** is shown in Figure 3 along with its numbering scheme. Selected bond distances and angles are reported in Table III.

The dinuclear $[Pt_2(\mu\text{-}H)(\mu\text{-}CO)(L\text{-}L)_2]^+$ cation, of C_2 idealized symmetry, contains two platinum atoms, which, if the Pt–Pt interaction is neglected, can be considered to be in a square-planar coordination, very distorted toward tetrahedral. With respect to the Pt(1), Pt(2), C plane the following out-of-plane displacements are observed: P(1) and P(2), −0.74 and +0.33 Å; P(3) and P(4),

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Table III. Selected Bond Distances (Å) and Angles (deg) with Their Esd's in Parentheses

(a) Within the $Pt_2P_4H(CO)$ Moiety			
Pt(1)–Pt(2)	2.790 (1)	Pt(1)–H	1.72 (7)
Pt(1)–P(1)	2.300 (2)	Pt(2)–H	1.72 (7)
Pt(1)–P(2)	2.358 (2)	Pt(1)–C	2.039 (8)
Pt(2)–P(3)	2.359 (2)	Pt(2)–C	2.004 (7)
Pt(2)–P(4)	2.293 (2)	C–O	1.182 (8)
P(1)–Pt(1)–P(2)	103.68 (6)	P(4)–Pt(2)–Pt(1)	133.45 (4)
P(3)–Pt(2)–P(4)	103.64 (6)	Pt(1)–Pt(2)–C	46.9 (2)
P(1)–Pt(1)–C	89.5 (2)	Pt(2)–Pt(1)–C	45.8 (2)
P(4)–Pt(2)–C	91.3 (2)	Pt(1)–C–Pt(2)	87.3 (3)
P(2)–Pt(1)–H	87 (2)	Pt(1)–C–O	135.1 (5)
P(3)–Pt(2)–H	86 (2)	Pt(2)–C–O	135.1 (6)
P(1)–Pt(1)–Pt(2)	132.30 (4)	P(2)–Pt(1)–C	166.2 (2)
P(2)–Pt(1)–Pt(2)	122.50 (4)	P(3)–Pt(2)–C	162.7 (2)
P(3)–Pt(2)–Pt(1)	121.45 (4)		
(b) Within the 1,1′-Bis(diphenylphosphino)ferrocene Ligands			
P(1)–C(111)	1.806 (6)	P(3)–C(311)	1.807 (6)
P(1)–C(121)	1.823 (7)	P(3)–C(321)	1.822 (6)
P(1)–C(131)	1.824 (8)	P(3)–C(331)	1.830 (6)
P(2)–C(211)	1.813 (7)	P(4)–C(411)	1.793 (6)
P(2)–C(221)	1.816 (7)	P(4)–C(421)	1.819 (7)
P(2)–C(231)	1.832 (6)	P(4)–C(431)	1.832 (6)
C(111)–C(112)	1.436 (9)	C(311)–C(312)	1.428 (8)
C(111)–C(115)	1.426 (10)	C(311)–C(315)	1.432 (9)
C(112)–C(113)	1.432 (10)	C(312)–C(313)	1.435 (9)
C(113)–C(114)	1.393 (12)	C(313)–C(314)	1.400 (10)
C(114)–C(115)	1.415 (10)	C(314)–C(315)	1.429 (8)
C(211)–C(212)	1.418 (11)	C(411)–C(412)	1.434 (9)
C(211)–C(215)	1.444 (10)	C(411)–C(415)	1.438 (8)
C(212)–C(213)	1.419 (11)	C(412)–C(413)	1.426 (9)
C(213)–C(214)	1.379 (14)	C(413)–C(414)	1.386 (10)
C(214)–C(215)	1.442 (12)	C(414)–C(415)	1.426 (9)
Fe(1)–C(111)	2.012 (6)	Fe(2)–C(311)	2.018 (6)
Fe(1)–C(112)	2.044 (7)	Fe(2)–C(312)	2.051 (7)
Fe(1)–C(113)	2.058 (7)	Fe(2)–C(313)	2.048 (7)
Fe(1)–C(114)	2.044 (8)	Fe(2)–C(314)	2.060 (7)
Fe(1)–C(115)	2.024 (7)	Fe(2)–C(315)	2.036 (7)
Fe(1)–C(211)	2.009 (6)	Fe(2)–C(411)	2.031 (6)
Fe(1)–C(212)	2.029 (8)	Fe(2)–C(412)	2.016 (6)
Fe(1)–C(213)	2.033 (9)	Fe(2)–C(413)	2.051 (7)
Fe(1)–C(214)	2.050 (8)	Fe(2)–C(414)	2.054 (7)
Fe(1)–C(215)	2.050 (8)	Fe(2)–C(415)	2.060 (6)
Fe(1)–C(av)	2.035	Fe(2)–C(av)	2.042
C(111)–C(112)–C(113)	107.7 (7)	C(311)–C(312)–C(313)	107.2 (6)
C(112)–C(113)–C(114)	107.8 (6)	C(312)–C(313)–C(314)	108.9 (6)
C(113)–C(114)–C(115)	109.5 (7)	C(313)–C(314)–C(315)	108.2 (6)
C(114)–C(115)–C(111)	107.8 (7)	C(314)–C(315)–C(311)	107.8 (6)
C(115)–C(111)–C(112)	107.3 (6)	C(315)–C(311)–C(312)	107.9 (5)
C(211)–C(212)–C(213)	106.6 (8)	C(411)–C(412)–C(413)	107.8 (6)
C(212)–C(213)–C(214)	109.9 (8)	C(412)–C(413)–C(414)	108.6 (6)
C(213)–C(214)–C(215)	108.9 (7)	C(413)–C(414)–C(415)	109.3 (6)
C(214)–C(215)–C(211)	105.4 (8)	C(414)–C(415)–C(411)	107.2 (6)
C(215)–C(211)–C(212)	109.1 (7)	C(415)–C(411)–C(412)	107.1 (5)
(c) Within the BF_4^- Anion			
B–F(1)	1.38 (1)	B–F(3)	1.37 (1)
B–F(2)	1.34 (1)	B–F(4)	1.30 (1)
F(1)–B–F(2)	106 (1)	F(2)–B–F(3)	112 (1)
F(1)–B–F(3)	106 (1)	F(2)–B–F(4)	113 (1)
F(1)–B–F(4)	109 (1)	F(3)–B–F(4)	112 (1)

+0.56 and −0.89 Å; O, +0.24 Å; H, +0.34 Å. The dihedral angles between the P–Pt–P and Pt–C–Pt planes are 19.2° (for Pt(1)) and 24.6° (for Pt(2)).

Extensive studies performed on complexes containing variously substituted ferrocenylphosphine ligands have shown a peculiarly large bite for this kind of diphosphine, resulting in quite large P–M–P angles: e.g. 99.3 (1)° in (L-L)$PtCl_2$,[15] 99.07 (5)° in (L-L)$PdCl_2$,[6c] and 96.82 (6)° in [(L-L)Rh(NBD)]$^+$.[7b] Correspondingly the average M–P distances (2.256 Å in (L-L)$PtCl_2$,[15] 2.292 or 2.284 Å in (L-L)$PdCl_2$[6c,16]) are large in comparison with the values observed in similar complexes with chelating diphosphines (e.g. 2.208[22] or 2.218 Å[23] in (DPE)$PtCl_2$ and 2.230 Å in (DPE)$PdCl_2$[24]). In the present cation the value of the P–M–P angle (average 103.66°) is the largest found in complexes with the L-L ligand and the Pt–P distances are again quite large (2.358 Å (trans to CO) and 2.296 Å (trans to H)).

An inspection of the intramolecular interactions in **8a** shows a very crowded situation toward the Pt(μ-H)(μ-CO)Pt core due to the bulkiness of the (diphenylphosphino)ferrocene ligands (shortest contacts O···C(131) = 2.992 (8) Å, O···C(436) = 3.009 (8) Å). Thus, the large values of the P–Pt–P angles seem rather unexpected, since the decrease of such an angle would probably relieve the overcrowding. Nevertheless, anomalously short contacts between the CO group and the phosphine phenyl rings are avoided through (i) a bending of the diphosphine ligands away from the bridging carbonyl toward the less sterically demanding bridging hydrogen atom (compare the values of 132.30 (4) and 133.45 (4)° for the P(1)–Pt(1)–Pt(2) and P(4)–Pt(2)–Pt(1) angles with 122.50(4) and 121.45 (4)° for P(2)–Pt(1)–Pt(2) and P(3)–Pt(2)–Pt(1)), (ii) a bending of the CO out of the Pt(1), Pt(2), C plane, (iii) a displacement of the phosphorus atoms from the coordination plane, and (iv) a lengthening of the Pt–Pt distance (2.790 (1) Å).

A comparison with the $[Pt_2(\mu\text{-H})(\mu\text{-CO})(DPE)_2]^+$ cation[12e] shows differences attributable to the different steric requirements of the phosphine ligands: (i) the P–Pt–P angle is only 87.1 (1)°, and the Pt–P distances are 2.321 (3) Å (trans to CO) and 2.264 (3) Å (trans to H); (ii) a minor displacement of the P atoms out of the Pt, Pt, C plane (−0.02 and +0.24 Å) is found; (iii) the Pt, C, O, Pt, H system is planar; (iv) the Pt–Pt distance is significantly shorter (2.716 (1) Å). As a consequence of the larger Pt–Pt distance (2.790 (1) Å) the present compound displays a greater Pt–C–Pt angle (87.3 (3) vs 84.6 (2)° in $[Pt_2(\mu\text{-H})(\mu\text{-CO})(DPE)_2]^+$), whereas the average Pt–C distance is the same (2.02 Å).

The platinum–ferrocenylphosphine moieties can be viewed as [3]ferrocenophanes in the half-chair conformation, with the cyclopentadienyl rings staggered.[16] The five-membered rings do not deviate significantly from planarity and only slightly from being parallel (the angle between the best planes of atoms C(111)–C(115) and C(211)–C(215) is 2.1°, and that between the planes C(311)–C(315) and C(411)–C(415) is 4.4°). P(1) and P(2) are 0.028 (2) and 0.044 (2) Å out of the cyclopentadienyl rings, both displaced toward Fe(1); P(3) is 0.062 (2) Å out toward Fe(2), and P(4) is 0.019 (2) Å away from Fe(2). The distances of the iron atoms from the planes of the cyclopentadienyl rings (1.639 and 1.635 Å for Fe(1) and 1.654 and 1.645 Å for Fe(2)) compare well with the values reported for other ferrocene moieties[25] and so do the distances Fe(1)–C(*i*1*j*) and Fe(2)–C(*i*1*j*), whose mean values are 2.035 and 2.042 Å, respectively, with a decrease of the spacing toward the P atoms. The pattern of bond distances within the cyclopentadienyl rings shows substituent-induced geometrical distortions with a mean C–C bond length for the P-substituted carbon atoms of 1.432 Å; the adjacent C–C bonds average 1.428 Å while the unique C–C bonds average 1.389 Å.

Experimental Section

The ligand 1,1′-bis(diphenylphosphino)ferrocene, aqueous HBF_4 (50%, *d* = 1.36 g/mL), and KBH_4 were purchased from Strem Chemicals, Inc., Hoechst, and Fluka, respectively. The platinum complex [(COD)$PtCl_2$] was prepared according to the literature.[26]

The analytical samples were pumped to constant weight (room temperature, ca. 0.1 Torr). Evaporation was always carried out under reduced pressure (water aspirator). The elemental analyses were performed by the Microanalytical Laboratories of the University of Milano and Sassari and by Mikroanalytisches Labor Pascher (Remagen, FRG).

Infrared spectra were recorded on Perkin-Elmer 1310 and Beckman 4210 spectrometers. ^1H (80 and 200.13 MHz), $^{13}C\{^1H\}$ (20.15 and 50.33 MHz), and $^{31}P\{^1H\}$ (32.4 and 81.015 MHz) NMR spectra were recorded on Bruker WP 80 and AC 200 spectrometers. The 2D experiments were

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Table IV. Fractional Atomic Coordinates with Their Esd's in Parentheses

atom	*x*	*y*	*z*
Pt(1)	−0.02174 (2)	0.22846 (2)	0.15118 (1)
Pt(2)	0.05418 (2)	0.20507 (2)	0.30728 (1)
Fe(1)	−0.16927 (8)	0.24630 (7)	−0.08483 (5)
Fe(2)	0.14135 (7)	0.24069 (6)	0.56891 (5)
P(1)	0.0726 (1)	0.2706 (1)	0.05159 (9)
P(2)	−0.2051 (1)	0.2424 (1)	0.10859 (9)
P(3)	−0.0689 (1)	0.1826 (1)	0.39962 (9)
P(4)	0.2312 (1)	0.2320 (1)	0.38739 (9)
F(1)	0.3920 (6)	0.6532 (4)	0.3825 (3)
F(2)	0.4218 (6)	0.7964 (4)	0.4202 (4)
F(3)	0.4345 (6)	0.7330 (5)	0.2932 (4)
F(4)	0.2683 (6)	0.7138 (7)	0.3297 (5)
O	0.1880 (4)	0.1681 (4)	0.1809 (3)
C	0.1178 (6)	0.1983 (5)	0.2051 (4)
B	0.3762 (9)	0.7267 (7)	0.3555 (6)
C(111)	−0.0015 (5)	0.2960 (4)	−0.0373 (3)
C(112)	−0.0191 (6)	0.2526 (5)	−0.1223 (4)
C(113)	−0.0846 (6)	0.2956 (5)	−0.1694 (4)
C(114)	−0.1046 (6)	0.3644 (5)	−0.1151 (4)
C(115)	−0.0544 (6)	0.3662 (5)	−0.0337 (4)
C(121)	0.1858 (5)	0.3747 (4)	0.0914 (4)
C(122)	0.2158 (6)	0.4147 (5)	0.1744 (4)
C(123)	0.2999 (7)	0.4944 (5)	0.2035 (5)
C(124)	0.3550 (7)	0.5353 (6)	0.1509 (6)
C(125)	0.3271 (8)	0.4970 (6)	0.0686 (6)
C(126)	0.2426 (7)	0.4171 (6)	0.0389 (4)
C(131)	0.1407 (6)	0.1890 (5)	0.0080 (4)
C(132)	0.2562 (7)	0.2041 (6)	0.0185 (5)
C(133)	0.3006 (7)	0.1369 (6)	−0.0142 (6)
C(134)	0.2347 (8)	0.0574 (6)	−0.0561 (5)
C(135)	0.1209 (9)	0.0392 (6)	−0.0668 (5)
C(136)	0.0732 (7)	0.1052 (5)	−0.0350 (5)
C(211)	−0.2572 (5)	0.2058 (5)	−0.0017 (4)
C(212)	−0.2320 (6)	0.1325 (5)	−0.0488 (4)
C(213)	−0.2827 (7)	0.1242 (6)	−0.1320 (5)
C(214)	−0.3382 (7)	0.1887 (7)	−0.1372 (4)
C(215)	−0.3246 (6)	0.2424 (6)	−0.0558 (4)
C(221)	−0.2183 (6)	0.3547 (4)	0.1358 (4)
C(222)	−0.1226 (6)	0.4250 (5)	0.1711 (5)
C(223)	−0.1316 (9)	0.5122 (6)	0.1916 (5)
C(224)	−0.2369 (9)	0.5254 (6)	0.1754 (5)
C(225)	−0.3331 (7)	0.4565 (6)	0.1419 (5)
C(226)	−0.3225 (7)	0.3721 (5)	0.1236 (5)
C(231)	−0.3214 (5)	0.1774 (4)	0.1465 (4)
C(232)	−0.3238 (6)	0.2010 (5)	0.2302 (4)
C(233)	−0.4104 (6)	0.1542 (5)	0.2606 (4)
C(234)	−0.4935 (6)	0.0834 (5)	0.2106 (4)
C(235)	−0.4918 (7)	0.0604 (6)	0.1297 (5)
C(236)	−0.4062 (7)	0.1075 (5)	0.0971 (4)
C(311)	−0.0150 (5)	0.1722 (4)	0.5016 (3)
C(312)	−0.0254 (5)	0.2202 (4)	0.5788 (4)
C(313)	0.0364 (5)	0.1907 (5)	0.6418 (4)
C(314)	0.0804 (6)	0.1242 (4)	0.6048 (4)
C(315)	0.0496 (5)	0.1119 (4)	0.5177 (4)
C(321)	−0.1331 (5)	0.2738 (4)	0.4177 (3)
C(322)	−0.0842 (6)	0.3511 (4)	0.3947 (4)
C(323)	−0.1322 (6)	0.4222 (5)	0.4050 (5)
C(324)	−0.2286 (7)	0.4152 (5)	0.4367 (5)
C(325)	−0.2764 (6)	0.3383 (5)	0.4603 (5)
C(326)	−0.2291 (6)	0.2680 (4)	0.4521 (4)
C(331)	−0.1850 (5)	0.0792 (4)	0.3640 (3)
C(332)	−0.2104 (6)	0.0330 (4)	0.2833 (4)
C(333)	−0.2976 (7)	−0.0461 (5)	0.2563 (4)
C(334)	−0.3593 (6)	−0.0800 (5)	0.3107 (5)
C(335)	−0.3333 (5)	−0.0352 (4)	0.3910 (4)
C(336)	−0.2470 (5)	0.0433 (4)	0.4182 (4)
C(411)	0.2472 (5)	0.2814 (4)	0.4943 (3)
C(412)	0.1955 (5)	0.3488 (4)	0.5240 (4)
C(413)	0.2290 (6)	0.3729 (4)	0.6114 (4)
C(414)	0.2967 (6)	0.3212 (5)	0.6358 (4)
C(415)	0.3111 (5)	0.2644 (4)	0.5649 (4)
C(421)	0.2793 (5)	0.1327 (4)	0.3833 (3)
C(422)	0.3912 (5)	0.1382 (4)	0.4167 (4)
C(423)	0.4265 (6)	0.0629 (5)	0.4138 (4)
C(424)	0.3509 (7)	−0.0195 (5)	0.3788 (5)
C(425)	0.2403 (7)	−0.0268 (5)	0.3469 (5)
C(426)	0.2026 (6)	0.0501 (4)	0.3484 (4)
C(431)	0.3455 (5)	0.3122 (4)	0.3608 (4)
C(432)	0.3773 (6)	0.4012 (5)	0.3985 (4)
C(433)	0.4627 (7)	0.4618 (5)	0.3756 (5)
C(434)	0.5159 (6)	0.4334 (5)	0.3165 (4)
C(435)	0.4856 (6)	0.3455 (5)	0.2792 (5)
C(436)	0.4019 (6)	0.2837 (5)	0.2994 (5)
OW	0.109 (1)	0.545 (1)	0.348 (1)
H	−0.064 (6)	0.206 (5)	0.240 (4)

performed on a Bruker AC 200 spectrometer by COSY-90 and homonuclear *J*-resolved methods.[27]

Pt(L-L)Cl$_2$ (1). (a) From K$_2$[PtCl$_4$]. The compound was prepared according to ref 26; yield 68%.

(b) From Pt(COD)Cl$_2$. A solution of the ligand (370 mg; 0.67 mmol) in chloroform (20 mL) was added to a stirred solution of Pt(COD)Cl$_2$ (250 mg, 0.66 mmol) in the same solvent (30 mL). After 1 h the crude product was obtained by concentration of the solution in the presence of a comparable volume of *n*-hexane. The product was crystallized from dichloromethane (20 mL) and *n*-hexane (20 mL): yield 85%; mp 335–340 °C (dec pt >250 °C). Anal. Calcd for $C_{34}H_{28}Cl_2FeP_2Pt$: C, 49.76; H, 3.41. Found: C, 49.35; H, 3.42. IR (Nujol; cm^{-1}): ν_{Pt-Cl} 315 s, 290 m. ^{13}C NMR (CDCl$_3$; ppm (*J* in Hz)): Cp rings, 73.5 d ($^1J_{PC_{ipso}}$ = 96), 73.85 and 75.95 (C_α and C_β; multiplets); Ph rings, 128.05 m (*o*-C), 131.31 s (*p*-C), 131.03 d ($^1J_{PC_{ipso}}$ = 67.4), 135.06 m (*m*-C). The assignments of ortho and meta carbons in the phenyl rings could be exchanged. For comparison the ^{13}C NMR spectrum of the ligand under the same conditions is as follows (ppm (*J* in Hz)): Cp rings, 76.8 d ($^1J_{PC_{ipso}}$ = 7.54), 73.9 d (C_α, $^2J_{PC}$ = 14.6), 72.6 (C_β, $^3J_{PC}$ = 2.6); Ph rings, 128.3 (*m*-C, $^3J_{PC}$ = 6.7), 128.6 s (*p*-C), 133.6 d (*o*-C, $^2J_{PC}$ = 19.3), 139.0 (ipso C, $^1J_{PC}$ = 9.7).

Pt(L-L)(pz)$_2$ (2) and Pt(L-L)(3,5-Me$_2$pz)$_2$ (3). The pyrazolato derivatives **2** and **3** were prepared from **1**, the appropriate pyrazole, and methanolic KOH according to a procedure already described.[12a] Typically, to a suspension of compound **1** (541 mg, 0.66 mmol) in methanol (60 mL) were added a solution of pyrazole (98 mg, 1.44 mmol) in the same solvent (30 mL) and 11 mL of methanolic KOH (0.128 M). After 1 h under reflux the clear solution was evaporated to dryness and the residue was crystallized from dichloromethane and *n*-hexane: yield 63% (**2**), 55% (**3**); dec pt >145 °C (**2**), >160 °C (**3**). Anal. Calcd for $C_{40}H_{34}FeN_4P_2Pt$ (**2**): C, 54.39; H, 3.85; N, 6.34. Found: C, 53.42; H, 4.01; N, 6.23. ^{13}C NMR (CDCl$_3$; ppm (*J* in Hz)): Cp rings, 73.2 d ($^1J_{PC_{ipso}}$ = 68), 75.8 and 73.6 (C_α and C_β, multiplets with line separations of 5.1 and 3.6 Hz, respectively); pz rings, 103.2 (4-C, $^3J_{PtC}$ = 30), 135.4 m (5-C, $^3J_{PC}$ = 2.67, $^2J_{PtC}$ = 52), 138.3 m (3-C, $^4J_{PC}$ = 3.8, $^3J_{PtC}$ = 55); Ph rings, 127.9 m (*o*-C), 130.6 s (*p*-C), 131 d ($^1J_{PC_{ipso}}$ = 65), 134.4 m (*m*-C). The assignments of ortho and meta carbons in the phenyl rings could be exchanged. Anal. Calcd for $C_{44}H_{42}FeN_4P_2Pt$ (**3**): C, 56.26; H, 4.47; N, 5.96. Found: C, 56.36; H, 4.72; N, 6.03. Mol wt: calcd, 938.8; found, 870 (3.440 mg/0.7253 g of CHCl$_3$).

[Pt(L-L)(3,5-Me-$_2$pzH)$_2$][BF$_4$]$_2$ (4). To a methanolic solution (20 mL) of compound **3** (95 mg, 0.101 mmol) was added a slight excess of aqueous HBF$_4$ (0.23 mmol) in the same solvent. After 10 min with stirring, the clear orange solution was evaporated to dryness and the residue dissolved in dichloromethane (10 mL). After addition of diethyl ether, the product was precipitated by concentration. The crude product was recrystallized from dichloromethane–diethyl ether, affording the analytical sample (45 mg): yield 40%; mp 225–230 °C (dec pt >200 °C). Anal. Calcd for $C_{44}H_{44}B_2F_8FeN_4P_2Pt$: C, 47.39; H, 3.95; N, 5.02. Found: C, 47.37; H, 4.04; N, 4.94.

[Pt(L-L)(H$_2$O)$_2$][BF$_4$]$_2$ (5). To a solution of compound **6** (360 mg, 0.21 mmol) in dichloromethane was added excess 35% aqueous HBF$_4$ (0.38 mL). After 15 min with stirring, the solution was evaporated to dryness and the residue was dissolved in benzene and evaporated to dryness. The procedure was carried out several times to remove excess water. The solid residue was collected and dried under vacuum (362 mg, yield 90%). Anal. Calcd for $C_{34}H_{32}B_2F_8FeO_2P_2Pt$: C, 42.54; H, 3.24. Found: C, 42.52; H, 3.25. IR (Nujol; cm^{-1}): 3540 w, br, 3200 w, br; 1630 w, br.

[Pt(L-L)(OH)]$_2$[BF$_4$]$_2$ (6). To a suspension of compound **1** (1.025 g, 1.25 mmol) in 100 mL of methanol was added a solution of AgBF$_4$ (484 mg, 2.48 mmol) in the same solvent (10 mL). After the mixture was

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stirred for 15 min, the solution was evaporated to dryness. The residue was extracted with three portions of dichloromethane; the solution was filtered and concentrated to a small volume. The crude product obtained by addition of diethyl ether, was crystallized from the same solvents to give the analytical sample (888 mg): yield 83%; dec pt >235 °C. Anal. Calcd for $C_{68}H_{58}B_2F_8Fe_2O_2P_4Pt_2$: C, 47.83; H, 3.63. Found: C, 48.08; H, 3.69. IR (Nujol; cm^{-1}): 3640 br, 3520 br, 3400 br, 1600 w, br.

$[Pt_2(L\text{-}L)_2H_3][BF_4]$ (7). (a) From Compound 4. To a stirred solution of compound **4** (549 mg, 0.492 mmol) in methanol (40 mL) was added finely ground KBH_4 (30 mg, 0.55 mmol) dissolved in 30 mL of the same solvent; a yellow precipitate was filtered and crystallized from dichloromethane (50 mL) and diethyl ether (50 mL) to give the yellow analytical sample by concentration (310 mg): yield 79%; mp 230 °C (dec >200 °C). Anal. Calcd for $C_{68}H_{59}BF_4Fe_2P_4Pt_2{\cdot}0.5CH_2Cl_2$: C, 50.45; H, 3.68. Found: C, 50.52; H, 3.91. IR (Nujol; cm^{-1}): 2035 w (ν_{PtH}).

(b) From Compound 6. Complex **7** was obtained similarly from the binuclear species **6**, by using a Pt/BH_4 molar ratio of 2/1; yield ca. 50%.

$[(L\text{-}L)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(L\text{-}L)][BF_4]$ (8). Complex **7** (406 mg, 0.856 mmol) was suspended in acetone (40 mL) and CO was bubbled into the suspension at room temperature for 30 min. The resulting red solution was evaporated to a small volume (ca. 10 mL) and eluted through a 20 × 1 cm column of deactivated Al_2O_3 (10% H_2O). The analytical sample (215 mg; yield 52%) was obtained by addition of diethyl ether to the concentrated solution: orange; mp 230–232 °C (dec >160 °C). Anal. Calcd for $C_{69}H_{57}BF_4Fe_2OP_4Pt_2$: C, 51.33; H, 3.53. Found: C, 51.54; H, 3.68. IR (Nujol; cm^{-1}): 1770 s (ν_{CO}).

X-ray Data Collection and Structure Determination. Crystal data and other experimental details are summarized in Table II. The diffraction experiment was carried out on a red prismatic crystal with an Enraf-Nonius CAD-4 diffractometer at room temperature, using monochromated Mo Kα radiation (λ = 0.71073 Å). The calculations were performed on a PDP 11/34 computer using the SDP-plus structure determination package.[28] The diffracted intensities were corrected for Lorentz effects, polarization, and absorption (empirical correction).[29] Scattering factors and anomalous dispersion corrections for atomic scattering factors of non-hydrogen atoms were taken from ref 30. No extinction correction was performed.

The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\sum w(F_o - k|F_c|)^2$. Anisotropic thermal factors were refined for Pt, Fe, P, O, F, and C atoms. A difference Fourier computed before the last cycles of the refinement revealed the positions of all the hydrogen atoms. A refinement of the bridging hydride was attempted and resulted in reasonable Pt-H distances and thermal parameter for the hydrogen atom. All the phosphinic hydrogens were introduced in the model at calculated positions (C-H = 0.95 Å).

The atomic coordinates of the structure model are listed in Table IV.

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Registry No. **1**, 104413-90-3; **2**, 118299-22-2; **3**, 118299-23-3; **4**, 118299-25-5; **5**, 118299-27-7; **6**, 111338-71-7; **7**, 118299-29-9; **8**, 118299-31-3; **8a**, 118299-32-4; L-L, 12150-46-8; $Pt(COD)Cl_2$, 12080-32-9; pzH, 288-13-1; 3,5-Me_2pzH, 67-51-6; $K_2[PtCl_4]$, 10025-99-7.

Supplementary Material Available: Tables of thermal parameters, calculated positions for hydrogen atoms, all bond distances and angles, and crystallographic details (29 pages); a listing of computed and observed structure factor moduli (44 pages). Ordering information is given on any current masthead page.

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Infrared Spectroscopic Studies on Metal Carbonyl Compounds. 24.[1] Observation of the Infrared Spectrum of an Acylrhodium Tetracarbonyl during the Hydroformylation of Olefins with Rhodium-Containing Catalyst Precursors

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An acylrhodium tetracarbonyl, $RC(O)Rh(CO)_4$, was observed and unambiguously identified by in situ infrared spectroscopy as an intermediate in the rhodium-catalyzed hydroformylation reaction at 25 °C. Its characteristic metal carbonyl ν(C–O) stretching frequencies occur at 2111 (27), 2065 (41), 2039 (65), and 2020 (100) cm^{-1} (with relative intensities in parentheses); the ν(C–O) of the acyl group could be observed at 1698 ± 3 cm^{-1} with R = $-(C_2H_4)C(CH_3)_3$, obtained from 3,3-dimethyl-1-butene as the starting olefin. The formation of this $RC(O)Rh(CO)_4$ species was observed both with $Rh_4(CO)_{12}$ and with $CoRh(CO)_7$ as catalyst precursors. The identified $RC(O)Rh(CO)_4$ is only stable at room temperature under at least 20 bar of carbon monoxide pressure.

Introduction

Alkyl- and acylcobalt tetracarbonyls were first prepared by Hieber and co-workers,[2] who also reported the easy uptake of carbon monoxide by alkylcobalt derivatives to form the corresponding acylcobalt compounds, as shown by eq 1. (The opposite

$$RCo(CO)_4 + CO \rightarrow RC(O)Co(CO)_4 \qquad (1)$$

reaction, i.e. the loss of the CO group of the acyl fragment, was observed only with fluoroorganic derivatives.) Subsequently, this step, playing an important role in the suggested mechanistic schemes of the catalytic cycles, was called "CO insertion", even if in some cases, e.g. for $CH_3Mn(CO)_5$, it has been shown[3] that the mechanism of the reaction is rather a methyl migration. In the case of other classes of metal carbonyls, however, as e.g. *cis*-$MX(CH_3)(CO)_2(PMe_3)_2$ (M = Fe, Ru; X = I, CH_3, etc.), it was demonstrated that the formation of an acetyl group from a methyl ligand proceeds effectively by cis insertion rather than by cis migration of the CH_3 group.[4]

The occurrence of these types of compounds in cobalt-catalyzed olefin hydroformylation[5] was first suggested by Sternberg and Wender and by Heck and Breslow.[6]

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