Steric Effects in the Chemistry of Platinum Cluster Complexes

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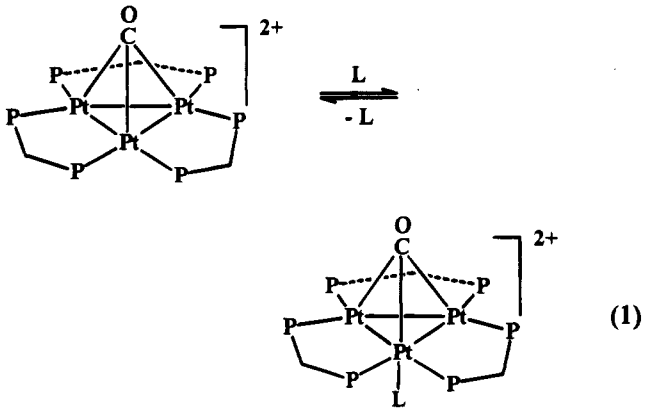
A study of steric effects of the ligands $R_2PCH_2PR_2$, R = aryl, on the formation and chemistry of the clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3(O_2CCF_3)]^+$, **4**, and $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$, **8**, is reported. When R = 2-MeC_6H_4, reduction of $[Pt(O_2CCF_3)_2(R_2PCH_2PR_2)]$ by CO/H_2O gave only the binuclear complex $[Pt_2H(CO)(\mu\text{-}R_2PCH_2PR_2)_2]^+$, but with smaller groups R, further reduction to **4** (R = 4-MeC_6H_4, 3-MeC_6H_4, 3,5-$Me_2C_6H_3$, 3,5-$F_2C_6H_3$, 3,5-$Cl_2C_6H_3$) or to $[Pt_4(\mu\text{-}CO)_2(\mu\text{-}H)(\mu\text{-}R_2PCH_2PR_2)_3(R_2PCH_2PR_2)]^+$ (R = 4-MeC_6H_4, 3,5-$F_2C_6H_3$) occurred. The complexes were characterized spectroscopically and for **4**(CF_3CO_2), R = 3,5-$Cl_2C_6H_3$, crystallographically [$C_{80}H_{42}Cl_{24}F_6O_5P_6Pt_3$·0.5$CH_2Cl_2$·1.5$H_2O$, monoclinic, $P2_1/n$, a = 23.365(4) Å, b = 24.599(4) Å, c = 19.141(7) Å, β = 102.44(2)°, Z = 4, R = 0.0727]. The complexes **8** can all form adducts with I^-, SCN^-, and $CF_3CO_2^-$ though evidence is presented that coordination of $CF_3CO_2^-$ is reversible in solution when R = 3,5-$Cl_2C_6H_3$. Reactions of **8** with the ligands L = PPh_3, $PMePh_2$, $P(OPh)_3$, and $P(OMe)_3$ to form the adducts $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3L]^{2+}$ are reversible, and the position of equilibrium depends on the steric effects of R, indicating the steric sequence R = 4-MeC_6H_4, 3-MeC_6H_4 < 3,5-$Me_2C_6H_3$ < 3,5-$F_2C_6H_3$ < 3,5-$Cl_2C_6H_3$.

Introduction

Steric effects of organophosphorus ligands can play an important role in the design of transition metal cluster complexes and in affecting their reactivity.[1,2] For example, the nuclearity and stoichiometry of platinum carbonyl phosphine clusters formed by reduction of platinum salts in the presence of CO and PR_3 depend critically on the steric bulk of the phosphine ligand PR_3.[3] More specifically, the reactions of the clusters $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ with PR_3 to give $[Pt_3(\mu\text{-}CO)_3(PR_3)_4]$ are less favorable with bulkier phosphines such as PCy_3 (Cy = cyclohexyl) than with smaller phosphines such as PPh_3.[3] Similarly, the addition of phosphine and phosphite ligands to $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (eq 1, dppm = $Ph_2PCH_2PPh_2$)is possible with ligands L with steric bulk



(1)

no greater than that of PPh_3.[4] In the above cluster, steric effects are between the incoming ligand and the phenyl substituents of the μ-dppm ligands, which define a cavity whose size is to some extent adjustable due to the flexibility of dppm.[4,5] However, increasing the cavity size on one side of the Pt_3 triangle of $Pt_3(\mu\text{-dppm})_3$ clusters, by moving phenyl substituents away, necessarily reduces the cavity size on the other side.[5] This paper describes attempts to determine how greatly these cavities could be tailored by modifying the supporting diphosphine ligands, $R_2PCH_2PR_2$. Most previous work in this area has concentrated on the ligand dppm, R = Ph, with some studies using dmpm (R = Me).[4-6] In the present work, the substituents used are substituted phenyl groups, chosen so that differences in electronic effects of the ligands should be relatively small while allowing major differences in steric bulk. The aim is to investigate in a systematic way how variation of the steric properties of the ligand $R_2PCH_2PR_2$ affects the formation and coordination chemistry of the clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$. These clusters are co-

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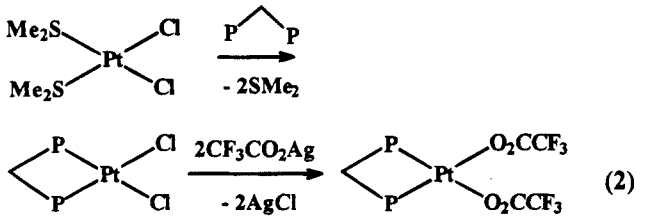
ordinatively unsaturated and can mimic some aspects of the reactivity of a platinum surface.[4]

Results

Synthesis and Characterization of Ligands and Simple Platinum Complexes. Several new diphosphine ligands $R_2PCH_2PR_2$, **1**, were prepared by reaction of $Cl_2PCH_2PCl_2$ with the corresponding Grignard reagent. The ligands were easily characterized by their NMR spectra. For example, each gave a singlet in the ^{31}P NMR with chemical shifts ranging from $\delta = -17.3$ to 46.6. These ligands and their NMR parameters are listed in Table 1.

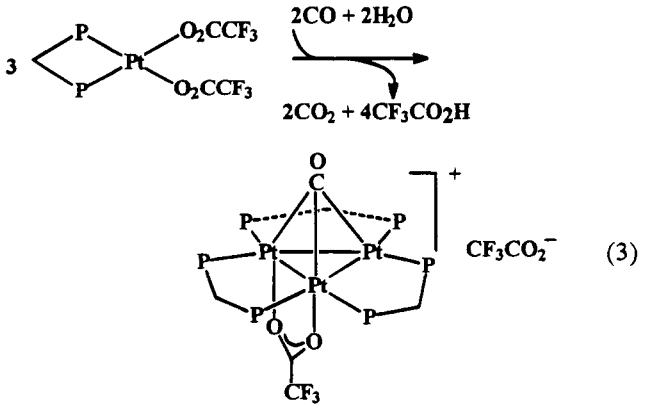
The above ligands were then used to prepare the mononuclear platinum complexes $[PtCl_2(R_2PCH_2PR_2)]$, **2**, and $[Pt(O_2CCF_3)_2(R_2PCH_2PR_2)]$, **3**, according to eq 2.



(2)

Most of the complexes **2** were very sparingly soluble; they were therefore easily isolated since they precipitated from the reaction mixtures in high yield, but most could not be characterized by NMR. However, complexes **3** were more soluble and NMR data were obtained. Each gave a singlet in the ^{31}P NMR with the ranges of $\delta(^{31}P) = -56.8$ to -92.2 and $^1J(PtP) = 3270-3450$ Hz. The chemical shifts are typical for chelating ligands of the type $R_2PCH_2PR_2$.[7] It is noted that the most sterically hindered complex **3g** gives the most negative value of $\delta(^{31}P)$ and the smallest value of $^1J(PtP)$ and that the compounds with electronegative substituents on the aryl groups **3e,f** give the least negative values of $\delta(^{31}P)$ and the largest values of $^1J(PtP)$. Full details of the NMR spectra are given in the Experimental Section, and selected parameters are in Table 1.

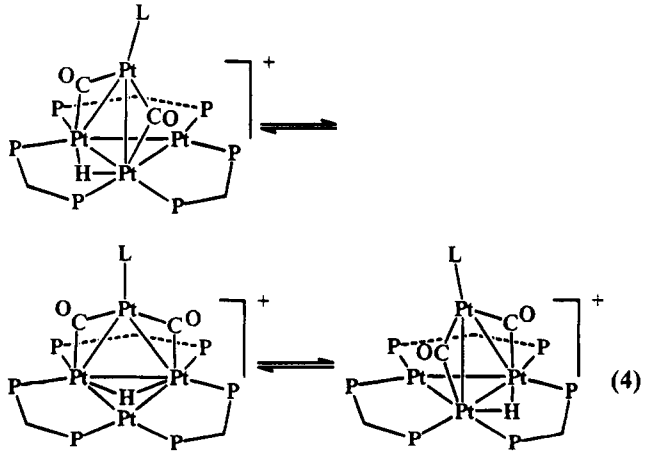
Reduction of the Platinum(II) Complexes. The reduction of the complexes $[Pt(O_2CCF_3)_2(R_2PCH_2PR_2)]$ under water gas shift (WGS) conditions to give $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3(O_2CCF_3)]^+$, **4**, as the trifluoroacetate salt, was carried out as reported for the case with R = Ph.[8] The reaction occurred with the stoichiometry shown in eq 3.



(3)

The reaction was successful in the cases with para or meta, but not with ortho, substituted phenyl derivatives R. When R = 2-MeC_6H_4, the product was the binuclear complex $[Pt_2H(CO)(\mu\text{-}R_2PCH_2PR_2)_2][CF_3CO_2]$, **5**, only, and this complex was stable to reduction to a triplatinum cluster. Unlike the corresponding dppm complex, it also failed to form an adduct with CO or to react with hydrogen to give the cation $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}R_2PCH_2PR_2)_2]^+$, **6**.[9,10] However, $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}R_2PCH_2PR_2)_2]^+$, R = 2-$MeC_6H_4$, prepared by reduction of **3c** with $NaBH_4$, did react with CO to form $[Pt_2H(CO)(\mu\text{-}R_2PCH_2PR_2)_2]^+$. It seems evident that the hydrido(carbonyl)diplatinum(I) complex is stabilized by the presence of the 2-methyl substituent, presumably by steric effects. In other cases, the binuclear diplatinum(I) complexes are intermediates in the formation of the clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3(O_2CCF_3)](O_2CCF_3)$ and the hydride $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}R_2PCH_2PR_2)_2]^+$ is more stable than $[Pt_2H(CO)(\mu\text{-}R_2PCH_2PR_2)_2]^+$.[9,10] For example, when R = 3,5-$Me_2C_6H_3$, an equilibrium mixture of $[Pt_2H(CO)(\mu\text{-}R_2PCH_2PR_2)_2]^+$ and $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}R_2PCH_2PR_2)_2]^+$ was detected at intermediate stages of reduction and, in the absence of CO, $[Pt_2H(CO)(\mu\text{-}R_2PCH_2PR_2)_2]^+$ was unstable, reacting with water to give $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}R_2PCH_2PR_2)_2]^+$.

In some cases, the reduction of the complexes **3** under WGS conditions led to tetranuclear products $[Pt_4(\mu_2\text{-}CO)_2(\mu_2\text{-}H)(\mu\text{-}R_2PCH_2PR_2)_3(R_2PCH_2PR_2)]^+$, **7**, isolated as the hexafluorophosphate salts.[11] These products reflect a degree of reduction beyond the clusters **4**. Their formation, although not completely predictable, was more likely under conditions where a buildup in the concentration of H_2 was allowed as a result of WGS catalysis, for smaller substituents R and for longer reduction times. The complexes with R = 4-MeC_6H_4 and R = 3,5-$F_2C_6H_3$ have been studied in depth. Both undergo the same form of fluxionality established previously for R = Ph (eq 4).[11] Details of the NMR spectra are given in the Experimental Section.



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Spectra and Structure of Clusters 4. The clusters **4** reacted with $NH_4[PF_6]$ to give the hexafluorophosphate salts $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3(O_2CCF_3)][PF_6]$

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Table 1. Selected NMR Data for the Ligands, 1, and Complexes, 3[a]

	compound			
	1		3	
R	$\delta(CH_2)$, J(PH)	δ(P)	$\delta(CH_2)$, J(PH), J(PtH)	δ(P), J(PtP)
4-MeC_6H_4, **a**	2.71, 3	−26.9	4.84, 11, 85	−70.2, 3319
3-MeC_6H_4, **b**	2.78, 1	−24.3	4.94, 12, 87	−68.3, 3324
2-MeC_6H_4, **c**	2.68, 3	−46.6	5.31, 11, 80	−71.4, 3304
3,5-$Me_2C_6H_3$, **d**	2.78, 0	−23.6	4.85, 11, 88	−68.6, 3319
3,5-$F_2C_6H_3$, **e**	2.80, 0	−17.3	5.36, 12, 91	−56.8, 3450
3,5-$Cl_2C_6H_3$, **f**	2.70, 0	−17.4	5.48, 12, 92	−57.2, 3450
2,4,6-$Me_3C_6H_2$, **g**	2.74, 0	−32.2	5.26, 11, 60	−92.2, 3270

[a] δ in ppm; J in Hz.

Table 2. Selected NMR and IR Data for Clusters 4 and 8[a]

R, compd	$\delta(CH^aH^b)$; $J(H^aH^b)$	δ(P), ^1J(PtP), ^3J(PP)	ν(CO)
4-MeC_6H_4, **4a**	5.6, 5.8; 14	−11.1, 3753, 155	1740
8a	5.5, 6.0; 16	−7.4, 3706, 138	1754
3-MeC_6H_4, **4b**	5.6, 5.7; 13	−11.2, 3741, 157	1734
8b	5.3, 5.4; 15	−6.8, 3701, 144	1734
3,5-$Me_2C_6H_3$, **4c**	5.3, 5.5; 12	−11.6, 3690, 160	1742
8c	5.2, 5.8; 14	−5.2, 3697, 139	1743
3,5-$F_2C_6H_3$, **4d**	5.7, 6.7; 13.3	−7.1, 3706, 161	1783
8d	5.9, 6.4; 14	0.4, 3759, 110	1784
3,5-$Cl_2C_6H_3$, **4e**	5.7, 6.6; 16	−8.4, 3673, 169	1771
8e	5.6, 6.5; 16	−8.4, 3672, 174	1771

[a] δ in ppm, J in Hz, ν in cm^{-1} (Nujol mull).

and, with excess $[PF_6]^-$, $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3][PF_6]_2$, **8**. Selected NMR and IR data for the clusters **4** and **8** are given in Table 2.

The values of ν(CO) for the triply bridging carbonyl ligand fall in the range 1734-1784 cm^{-1} and are similar for clusters **4** and **8**. The highest values of ν(CO) are observed for R = 3,5-$F_2C_6H_3$ and 3,5-$Cl_2C_6H_3$, the aryl groups with electron-withdrawing substituents. This suggests that ν(CO) is mostly influenced by electronic effects of the ligands, as would be expected.

The ^1H NMR spectra of complexes **4** and **8** are similar, but there were differences in the ^{31}P NMR spectra. In general, the ^{31}P chemical shifts of clusters **4** were 3−7 ppm more negative than for the corresponding clusters **8**.[8,12] The only exception was for R = 3,5-$Cl_2C_6H_3$ for which the ^{31}P chemical shifts of **4e** and **8e** were identical. This is interpreted in terms of dissociation of trifluoroacetate from **4e** in solution to give the cluster **8e**, promoted by the bulky substituents.

In the idealized structure of **8**, the cluster has 3-fold symmetry and so should give a single resonance for the $R_2PCH_2PR_2$ ligands.[5] The symmetry of **4** is lower, but since the ligated trifluoroacetate is weakly held, fluxionality is easy and leads to effective 3-fold symmetry. In agreement with this picture the clusters **4a−d** and **8a−d** all give a single resonance in the ^{31}P NMR spectra in the diphosphine ligand region at either room temperature or at −80 °C. However, while the room temperature spectra of **4e** and **8e** give a single ^{31}P resonance, at low temperature the resonance splits into three equal intensity resonances (Figure 1). The low-temperature spectra of **4e** and **8e** and the coalescence temperature are the same within experimental error, suggesting that the ion in solution is the same, namely the dication **8e**, in both cases. Clearly, the cluster with

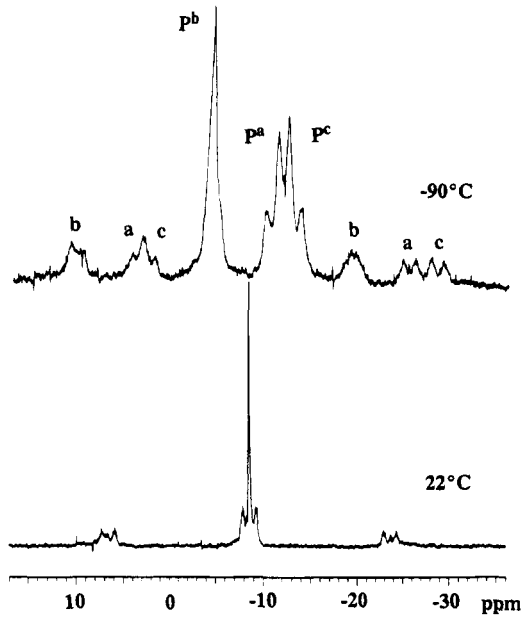

Figure 1. ^{31}P NMR spectra (121.47 MHz) of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$, R = 3,5-$Cl_2C_6H_3$, **4e**, at −90 °C and at 22 °C.

R = 3,5-$Cl_2C_6H_3$ is the most sterically hindered of those studied and it seems that steric effects lead to easy dissociation of the trifluoroacetate ligand from **4e**. In addition, the ground state structure of **8e** must have lower symmetry than C_{3v} and the bulky substituents give rise to a higher activation energy for flexing of the $R_2PCH_2PR_2$ ligands than in the other cases. Hence the variable-temperature NMR spectra can be understood.

In order to understand these effects, an X-ray structure determination of **4e** as the trifluoroacetate salt was carried out. Selected bond distances and angles are given in Table 3, and atomic coordinates are in Table 4. A view of the structure is given in Figure 2, and the steric effects are illustrated by the space-filling models in Figure 3.

The structure of **4e** is based on an approximately equilateral triangular Pt_3 metal core, with Pt−Pt distances 2.603(1), 2.610(1), and 2.624(1) Å and Pt−Pt−Pt angles 59.76(4), 59.89(4), and 60.46(3)°. The mean Pt−Pt distance (2.61(1) Å) is slightly shorter than that (2.63(2) Å) found in the $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ and indicates the presence of Pt−Pt single bonds.[8] Each edge of the Pt_3 triangle is bridged by a diphosphine ligand, and the Pt−P distances have a mean value of 2.29(2) Å, slightly longer than that of 2.28(1) Å in $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$.[8] One face of the Pt_3 triangle is bridged by a μ_3-CO ligand, and the other, by a weakly bound μ_2-trifluoroacetate ligand. All three $R_2PCH_2PR_2$ methylene carbon atoms C(10), C(20), and C(30) are folded away from the triply bridging carbonyl, being displaced from the Pt_3 plane by 0.80, 0.78, and 1.10 Å, respectively. In this conformation, all dichlorophenyl substituents on the carbonyl and CF_3CO_2 sides of the Pt_3 plane are axial and equatorial, respectively. This arrangement leads to a larger cavity on the trifluoroacetate side of the cluster, as is necessary to accommodate the larger group (Figure 3). It also gives rise to a structure in which all the phenyl rings are paired, with each pair lying essentially parallel. Thus, there are three pairs of parallel dichlorophenyl rings on each side of the Pt_3 triangle. The distances between the parallel phenyl rings range from 3.2(1) to 3.6(1) Å,

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Table 3. Selected Bond Distances (Å) and Angles (deg) for 4e

Pt(1)–Pt(2)	2.610(1)	Pt(1)–Pt(3)	2.603(1)
Pt(1)–P(1)	2.301(6)	Pt(1)–P(6)	2.286(6)
Pt(1)–C(1)	2.04(2)	Pt(1)–O(2)	2.52(2)
Pt(2)–Pt(3)	2.624(1)	Pt(2)–P(2)	2.324(6)
Pt(2)-P(3)	2.286(6)	Pt(2)–C(1)	2.06(2)
Pt(2)–O(3)	2.52(2)	Pt(3)–P(4)	2.276(6)
Pt(3)–P(5)	2.282(6)	Pt(3)–C(1)	2.24(2)
P(1)–C(10)	1.73(2)	P(2)–C(10)	1.88(2)
P(3)–C(2)	1.80(2)	P(4)–C(20)	1.81(2)
P(5)–C(30)	1.80(2)	P(6)–C(30)	1.81(2)
C(1)–O(1)	1.20(2)	O(2)–C(2)	1.20(3)
O(3)–C(2)	1.21(3)	C(2)–C(3)	1.54(3)
C(3)–F(1)	1.23(4)	C(3)–F(2)	1.24(4)
C(3)–F(3)	1.24(5)		
Pt(2)–Pt(1)–Pt(3)	60.46(3)	Pt(2)–Pt(1)–P(1)	95.4(2)
Pt(2)–Pt(1)–P(6)	155.0(2)	Pt(2)–Pt(1)–C(1)	50.9(6)
Pt(2)–Pt(1)–O(2)	85.2(4)	Pt(3)–Pt(1)–P(1)	155.9(2)
Pt(3)–Pt(1)–P(6)	94.6(2)	Pt(3)–Pt(1)–C(1)	56.1(6)
Pt(3)–Pt(1)–O(2)	87.6(5)	P(1)–Pt(1)–P(6)	109.6(2)
P(1)–Pt(1)–C(1)	110.0(7)	P(1)–Pt(1)–O(2)	90.5(5)
P(6)–Pt(1)–C(1)	118.4(7)	P(6)–Pt(1)–O(2)	92.4(4)
C(1)–Pt(1)–O(2)	131.7(7)	Pt(1)–Pt(2)–Pt(3)	59.76(4)
Pt(1)–Pt(2)–P(2)	95.2(2)	Pt(1)–Pt(2)–P(3)	154.7(2)
Pt(1)–Pt(2)–C(1)	50.1(7)	Pt(1)–Pt(2)–O(3)	84.7(4)
Pt(3)–Pt(2)–P(2)	154.3(2)	Pt(3)–Pt(2)–P(3)	95.0(2)
Pt(3)–Pt(2)–C(1)	55.5(6)	Pt(3)–Pt(2)–O(3)	84.6(4)
P(2)–Pt(2)–P(3)	109.9(2)	P(2)–Pt(2)–C(1)	113.9(7)
P(2)–Pt(2)–O(3)	88.0(5)	P(3)–Pt(2)–C(1)	118.2(7)
P(3)–Pt(2)–O(3)	92.4(4)	C(1)–Pt(2)–O(3)	129.5(7)
Pt(1)–Pt(3)–Pt(2)	59.89(4)	Pt(1)–Pt(3)–P(4)	155.2(2)
Pt(1)–Pt(3)–P(5)	94.9(2)	Pt(1)–Pt(3)–C(1)	49.1(6)
Pt(2)–Pt(3)–P(4)	95.5(2)	Pt(2)–Pt(3)–P(5)	151.9(2)
Pt(2)–Pt(3)–C(1)	49.4(6)	P(4)–Pt(3)–P(5)	108.3(2)
P(4)–Pt(3)–C(1)	118.4(6)	P(5)–Pt(3)–C(1)	124.5(6)

Table 4. Selected Atomic Coordinates and Thermal Parameters (Å²) for 4e

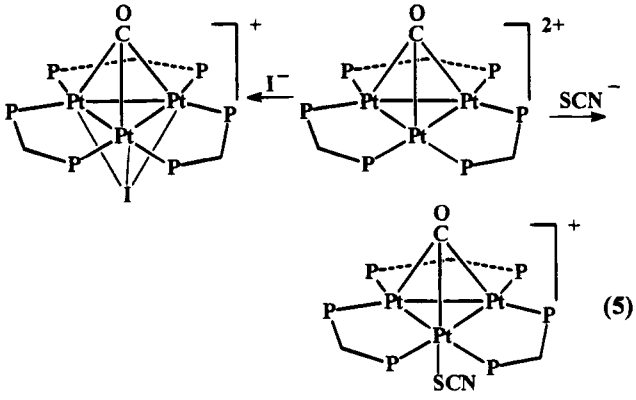
atom	*x*	*y*	*z*	B_{iso}
Pt(1)	0.24440(4)	0.80939(4)	0.10114(5)	2.76(4)
Pt(2)	0.24205(4)	0.70500(4)	0.07642(5)	2.76(4)
Pt(3)	0.27328(4)	0.77299(4)	−0.01426(5)	2.98(4)
P(1)	0.2142(3)	0.8029(2)	0.2076(3)	3.0(3)
P(2)	0.2019(3)	0.6821(3)	0.1735(3)	3.1(3)
P(3)	0.2514(2)	0.6289(2)	0.0112(3)	3.0(3)
P(4)	0.2841(2)	0.7085(3)	−0.0956(3)	3.0(3)
P(5)	0.2701(3)	0.8561(3)	−0.0680(3)	3.2(3)
P(6)	0.2559(3)	0.8988(2)	0.0748(3)	2.9(3)
C(10)	0.1704(10)	0.7458(9)	0.2044(13)	3.9(5)
C(20)	0.2425(9)	0.6488(9)	−0.0813(11)	3.3(5)
C(30)	0.2326(9)	0.9034(9)	−0.0217(10)	3.0(4)
C(1)	0.3124(10)	0.7574(9)	0.1014(12)	3.8(5)
O(1)	0.3627(6)	0.7511(6)	0.1303(8)	3.6(3)
O(2)	0.1393(8)	0.8083(8)	1.0327(10)	7.1(5)
O(3)	0.1396(8)	0.7226(7)	1.0064(10)	6.2(4)
C(2)	0.1172(8)	0.7670(8)	1.0060(13)	5.6(6)
C(3)	0.0518(8)	0.7699(11)	0.9692(15)	11.3(13)
F(1)	0.0253(10)	0.7294(14)	0.9835(21)	20.2(30)
F(2)	0.0446(10)	0.7713(16)	0.9031(13)	18.8(29)
F(3)	0.0290(12)	0.8125(16)	0.9844(22)	33.9(45)

indicating weak π-stacking of the paired aryl rings. As a consequence, the structure has approximate C_s symmetry, the mirror plane passing through Pt(3), C(1), and the midpoint of the Pt(1)–Pt(2) bond. The phosphorus atoms P(1), P(2), P(3), P(4), P(5), and P(6) are displaced from the Pt_3 plane away from the μ_3-CO ligand by 0.001, 0.226, 0.041, 0.123, 0.516, and 0.076 Å, respectively. The largest distortion involves the phosphorus atoms P(4) and P(5) which coordinate to Pt(3). The carbonyl ligand adopts a slightly distorted, triply bridging geometry, binding more strongly to Pt(1) and Pt(2) than to Pt(3) with the Pt–C distances 2.04(2), 2.06(2), and 2.24(2) Å, respectively. The shorter bonds are to the two platinum atoms bridged by the trifluoroacetate ligand. The trifluoroacetate is weakly bonded as indicated by the long Pt–O distances, both 2.52(2) Å; most Pt–O single bonds fall in the range 2.0–2.2 Å. For example, in cluster complexes, Pt–O distances ranging 2.01–2.14 Å are seen in $[Pt_4(\mu\text{-}CCl_3COO)_4(\mu\text{-}CH_3COO)_4]$,[13] and distance ranging 1.97–2.19 Å, in $[Pt_4(CH_3COO)_8]$.[14] The calculated Pauling covalent Pt–O bond length is 2.03 Å. The observation of weak Pt···O bonds in **4e** is clearly consistent with the hypothesis, outlined earlier, that the trifluoroacetate ligand dissociates in solution to give **8e**.

By reference to the structure of **4e**, the phosphorus atoms could be assigned to the pairs P(1), P(2); P(3), P(6); and P(4), P(5). If a similar conformation is present in **8e**, this would be consistent with the low-temperature ^{31}P NMR spectrum which contains three resonances. However, it must be recognized that dissociation of the CF_3CO_2 ligand is likely to lead to a change in conformation.

Coordination Chemistry of the Triplatinum Clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$. The cluster $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$ has a 42-electron count with each platinum having a 16-electron configuration. Hence each platinum atom is coordinatively unsaturated and the cluster is expected to form coordination complexes, although steric effects of the ligands $R_2PCH_2PR_2$ may limit the ability of the cluster to bind bulky donor ligands.

Clusters **8**, as the $[PF_6]^-$ salts, all react readily with MeI or NaI to form the clusters $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}I)(\mu\text{-}R_2PCH_2PR_2)_3]^+$, **9**, according to eq 5. Similarly, all reacted with thiocyanate to form the adducts $[Pt_3(\mu_3\text{-}CO)(SCN)(\mu\text{-}R_2PCH_2PR_2)_3]^+$, **10**. The corresponding reactions with R = Ph have been established earlier.[5,15]



(5)

Steric discrimination was most clearly observed with phosphite and phosphine ligands. It is known that reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ with $P(OR)_3$ (R = Me or Ph) gives a thermally stable adduct $[Pt_3(\mu_3\text{-}CO)(P(OR)_3)(\mu\text{-}dppm)_3]^{2+}$ but that, with the bulkier ligand PPh_3, adduct formation is reversible and the product cannot be isolated.[4] Reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$, **8**, with $P(OPh)_3$ at low temperature gave the adducts $[Pt_3(\mu_3\text{-}CO)\{P(OPh_3\}(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$ (**9**) (eq 1, L = $P(OPh)_3$) when R = 4-MeC_6H_4, 3-MeC_6H_4, 3,5-$Me_2C_6H_3$, and 3,5-$F_2C_6H_3$, as monitored by ^{31}P NMR spectroscopy, but no reaction occurred in the case of R

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(14) De Carrondo, C. T.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1976**, 410.
(15) Ferguson, G.; Lloyd, B. R.; Manojlovic-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4190.

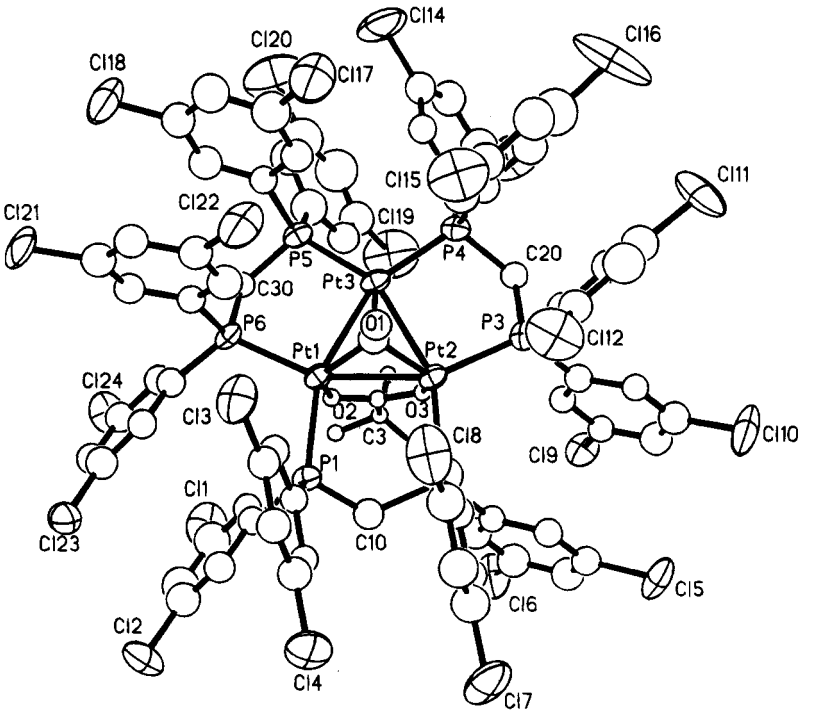

Figure 2. View of the structure of the cation $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3(O_2CCF_3)]^+$, R = 3,5-$Cl_2C_6H_3$, **4e**, showing 50% probability ellipsoids and the atom-labeling scheme. Atoms of the CF_3CO_2 group are shown as spheres of arbitrary radius, and hydrogen atoms are omitted for clarity.

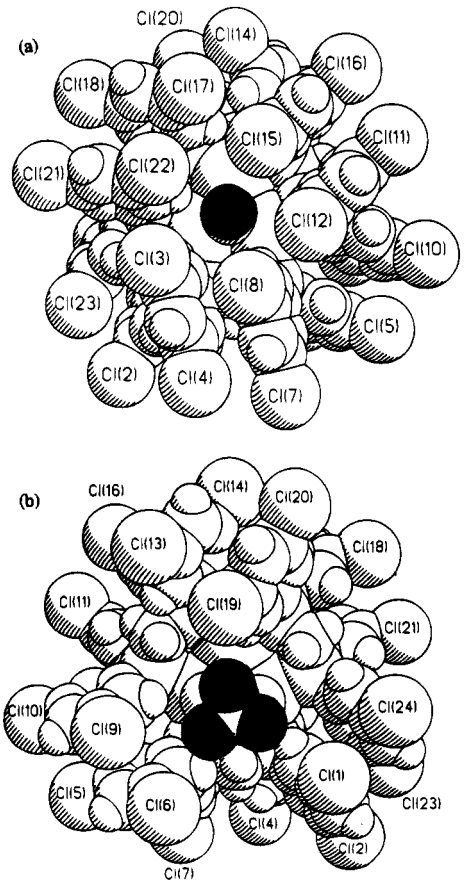

Figure 3. Space filling models of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3(O_2CCF_3)]^+$, R = 3,5-$Cl_2C_6H_3$, **4e**, (a) on the carbonyl side (the carbonyl O atom is shaded) and (b) on the trifluoroacetate side (the F atoms are shaded) of the Pt_3 triangle.

= 3,5-$Cl_2C_6H_3$. These reactions are reversible, and the position of the equilibrium depends on the bulk of R. In the case of R = 3,5-$Me_2C_6H_3$ and 3,5-$F_2C_6H_3$, the adducts **9** existed only at low temperature and fully dissociated to the corresponding starting material **8** and $P(OPh)_3$ at room temperature. In the case of 4-MeC_6H_4 and 3-MeC_6H_4, the adducts dissociated partially at room temperature. The reactions of **8**, with R = 3,5-$F_2C_6H_3$ and 3,5-$Cl_2C_6H_3$, with the less bulky ligand $P(OMe)_3$ were also studied. Both gave adducts at low temperature, but at room temperature, the adduct dissociated completely to the starting materials when R = 3,5-$Cl_2C_6H_3$ but only partially when R = 3,5-$F_2C_6H_3$ as determined by ^{31}P NMR.[4] When L is the larger phosphine $PMePh_2$, reversible coordination is detected when R = 3,5-$Me_2C_6H_3$ but not when R = 3,5-$F_2C_6H_3$ or 3,5-$Cl_2C_6H_3$.

Discussion

The role of steric effects of the diphosphine ligands on the formation and chemistry of clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$ has been established, using substituted phenyl substituents R. In the case of the ortho-substituted derivative, R = 2-MeC_6H_4, the steric effects of the ligand $R_2PCH_2PR_2$ are so great that formation of the corresponding triplatinum cluster is not possible and only dinuclear complexes can be formed.[9,10] With *meta*- and *para*-substituted phenyl groups R, the triplatinum clusters are formed and, in several cases, can be further converted to tetraplatinum clusters.[11] The ease of the conversion to the Pt_4 cluster is greater with less bulky $R_2PCH_2PR_2$ ligands, following the sequence R = 4-MeC_6H_4 ~ 3-MeC_6H_4 > 3,5-$Me_2C_6H_3$ ~ 3,5-$F_2C_6H_3$ > 3,5-$Cl_2C_6H_3$. The greater steric effects with R = 3,5-$Cl_2C_6H_3$, are also responsible for the cluster $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$ giving three resonances in the low-temperature ^{31}P NMR spectrum, whereas only one such resonance is observed in all other cases. The coordination of the anions I^- and SCN^- to the triplatinum clusters **8** occurs in all cases, but with the ligands PPh_3, $PMePh_2$, $P(OR)_3$, and $CF_3CO_2^-$, there

is evidence for steric effects, which are greatest when R = 3,5-$Cl_2C_6H_3$. In this case, the cavity size, defined by the $R_2PCH_2PR_2$ ligands of the $Pt_3(\mu\text{-}R_2PCH_2PR_2)_3$ triangle, is so small that the $P(OPh)_3$ ligand does not bind but is still large enough to bind $P(OMe)_3$ at low temperature. Thus from experiments of this kind using phosphines and phosphites with different cone angles, it was determined that the steric effects of the $R_2PCH_2PR_2$ ligand to the triplatinum clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$ are in the order 2-MeC_6H_4 > 3,5-$Cl_2C_6H_3$ > 3,5-$F_2C_6H_3$ > 3,5-$Me_2C_6H_3$ > 3-MeC_6H_4, 4-MeC_6H_4, C_6H_5. This assumes that electronic effects can be neglected. Although the electron density at the Pt_3 center is unlikely to change to a major extent, there is evidence from the value of $\nu(\mu_3\text{-CO})$ that minor changes can occur. It is also possible that electronic effects between fluoro or chloro substituents when R = 3,5-$F_2C_6H_3$ or 3,5-$Cl_2C_6H_3$ and the incoming ligands L might be significant in some cases. However, it is clear that the major effects on the ability to form the clusters, and on their ability to bind phosphine and phosphite ligands in particular, arise from steric effects of the substituents R. The cavity size can indeed be tailored and does lead to size selectivity in ligand binding.

Experimental Section

All reactions were performed under N_2 atmosphere using standard Schlenk techniques unless otherwise noted. All solvents were dried and distilled before use. The phosphine ligand $Cl_2PCH_2PCl_2$ was prepared using established methods.[16] NMR spectra were recorded by using a Varian Gemini-300 instrument. The proton and carbon chemical shifts are positive downfield relative to external Me_4Si. $^{31}P\{^1H\}$ NMR spectra are externally referenced to 85% H_3PO_4, with downfield chemical shifts reported as positive.

$R_2PCH_2PR_2$. A solution of 4-MeC_6H_4MgBr was prepared from 4-MeC_6H_4Br (22.6 mL, 0.184 mol) with Mg (4.46 g, 0.184 mol) in dry ether (50 mL), initiating the reaction with $C_2H_4Br_2$ (1 mL). The above solution was cooled to −7 °C, and a solution of $Cl_2PCH_2PCl_2$ (6.15 mL, 0.0459 mL) in ether (10 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 15 h and then cooled to −7 °C and hydrolyzed by addition of saturated aqueous NH_4Cl (40 mL). The mixture was added to a solution of KOH (100 g) in water (300 mL) in a liquid−liquid continuous extractor. Ether (200 mL) was added, and the product was extracted for 12 h. The ether extract was dried over $MgSO_4$, and the ether was evaporated to give $\{(4\text{-}MeC_6H_4)_2P\}_2CH_2$ as a yellow oil in 70% yield. A part was recrystallized from CH_2Cl_2/EtOH as colorless crystals. NMR in $CDCl_3$: $\delta(^1H)$ = 7.29 [m, 8H, ^3J(HH) = 8 Hz, ^4J(HH) = 3 Hz, aryl], 7.08 [d, 8H, ^3J(HH) = 8 Hz, aryl], 2.71 [t, 2H, ^2J(PH) = 3 Hz, CH_2P_2], 2.30 [t, 12 H, ^4J(HH) = 3 Hz, Me]; $\delta(^{31}P)$ = −26.9 [s, P].

Similarly were prepared the following compounds. R = 3-MeC_6H_4: yield 65%; NMR in $CDCl_3$ $\delta(^1H)$ = 7.1−7.4 [m, 16H, aryl], 2.78 [t, 2H, ^2J(PH) = 1 Hz, CH_2P_2], 2.26 [s, 12H, Me], $\delta(^{31}P)$ = −24.3 [s, P]. R = 2-MeC_6H_4: yield 45%; NMR in $CDCl_3$ $\delta(^1H)$ = 7.1−7.3 [m, 16H, aryl], 2.68 [t, 2H, ^2J(PH) = 3 Hz, CH_2P_2], 2.28 [s, 12H, Me], $\delta(^{31}P)$ = −46.6 [s, P]. R = 3,5-$Me_2C_6H_3$: yield 60%; NMR in $CDCl_3$ $\delta(^1H)$ = 7.18 [s, 4H, aryl], 6.88 [d, 8H, ^3J(PH) = 24 Hz, aryl], 2.78 [s, 2H, CH_2P_2], 2.27 [s, 24H, Me], $\delta(^{31}P)$ = −23.6 [s, P]. R = 2,4,6-$Me_3C_6H_2$: yield 70%; NMR in $CDCl_3$ $\delta(^1H)$ = 6.76 [s, 8H, aryl], 2.74 [s, 2H, CH_2P_2], 2.24, 2.33 [br s, 36H, Me], $\delta(^{31}P)$ = −32.2 [s, P]. The following compounds were prepared similarly, except that the reaction mixtures were extracted with ether using standard Schlenk techniques. R = 3,5-$Cl_2C_6H_3$: yield 82%; NMR in $CDCl_3$ $\delta(^1H)$ = 7.4−6.9 [m, 12H, $C_6\boldsymbol{H_3}$], 2.70 [br s, 2H, $C\boldsymbol{H_2}P_2$], $\delta(^{31}P)$ = −17.4 [s]. R = 3,5-$F_2C_6H_3$: yield 85%; NMR in $CDCl_3$ $\delta(^1H)$ = 7.3−6.8 [m, 12H, $C_6\boldsymbol{H_3}$], 2.80 [br s, 2H, $C\boldsymbol{H_2}P_2$], $\delta(^{31}P)$ = −17.3 [s].

$[PtCl_2(R_2PCH_2PR_2)]$. To a stirred solution of a mixture of *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ (2.67 g, 6.84 mmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of $R_2PCH_2PR_2$ (R = 3,5-$Cl_2C_6H_3$, 6.84 mmol) in CH_2Cl_2 (10 mL). A white precipitate formed immediately. After 6 h, the product was collected by filtration and washed with diethyl ether (10 mL) and pentane (10 mL) and dried under vacuum. Yield: 93%. Anal. Calcd for $C_{25}H_{14}Cl_{10}P_2Pt$: C, 32.43; H, 1.51. Found: C, 32.33; H, 1.27. NMR: insufficient solubility.

Similarly were prepared the following compounds. R = 3,5-$F_2C_6H_3$: yield 95%. Anal. Calcd for $C_{25}H_{14}Cl_2F_8P_2Pt$: C, 37.80; H, 1.78. Found: C, 38.12; H, 1.90. NMR: insufficient solubility. R = 4-MeC_6H_4: yield 88%. Anal. Calcd for $C_{29}H_{30}Cl_2P_2Pt$: C, 49.3; H, 4.3. Found: C, 48.9; H, 4.1. NMR in $CDCl_3$: $\delta(^1H)$ = 7.05, 7.83 [m, 16H, aryl], 4.54 [t, 2H, ^2J(PH) = 14 Hz, ^3J(PtH) = 70 Hz, CH_2P_2], 2.21 [s, 12H, Me]; $\delta(^{31}P)$ = −68.6 [s, ^1J(PtP) = 3078, P]. R = 3,5-$Me_2C_6H_3$: yield 35%. Anal. Calcd for $C_{33}H_{38}Cl_2P_2Pt$: C, 52.0; H, 5.0. Found: C, 51.0; H, 5.3. NMR: insufficient solubility. R = 2-MeC_6H_4: yield 75%. Anal. Calcd for $C_{29}H_{30}Cl_2P_2Pt$: C, 49.3; H, 4.3. Found: C, 49.0; H, 4.6. NMR in $CDCl_3$: $\delta(^1H)$ = 7.53−8.07 [m, 16H, aryl], 5.15 [t, 2H, ^2J(PH) = 11 Hz, ^3J(PtH) = 68 Hz, CH_2P_2], 2.31 [s, 12H, Me]; $\delta(^{31}P)$ = −64.6 [s, ^1J(PtP) = 3068, P]. R = 2,4,6-$Me_3C_6H_2$: yield 25% Anal. Calcd for $C_{37}H_{46}Cl_2P_2Pt$: C, 54.3; H, 5.7. Found: C, 54.2; H, 5.9. NMR in $CDCl_3$: $\delta(^1H)$ = 6.78 [s, 8H, aryl], 5.23 [t, 2H, ^2J(PH) = 10 Hz, ^3J(PtH) = 51 Hz, CH_2P_2], 2.24 [s, 12H, Me], 2.39 [s, 24H, Me]; $\delta(^{31}P)$ = −83.8 [s, ^1J(PtP) = 3089, P].

$[Pt(O_2CCF_3)_2(R_2PCH_2PR_2)]$. To a stirred suspension of $[PtCl_2(R_2PCH_2PR_2)]$, R = 3,5-$Cl_2C_6H_4$ (1.05 g, 1.13 mmol), in acetone (25 mL) and trifluoroacetic acid (2 mL) was added silver trifluoroacetate (0.55 g, 2.5 mmol). The mixture was stirred at room temperature in the dark for 1 h and then refluxed for 3 h. The mixture was cooled to room temperature and filtered to remove the AgCl precipitate, and the solvent was evaporated under vacuum to give a yellow oil, which was triturated with ether at 0 °C to give the product as a white solid. Yield: 86%. Anal. Calcd for $C_{29}H_{14}Cl_8F_6O_4P_2Pt$: C, 32.22; H, 1.31. Found: C, 32.41; H, 1.42. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 8.10−8.02 [m, 8H, aryl], 7.8 [t, 4H, ^4J(HH) = 2 Hz, aryl], 5.48 [t, 2H, ^2J(PH) = 12 Hz, ^3J(PtH) = 92.5 Hz, $C\boldsymbol{H_2}P_2$]; $\delta(^{31}P)$ = −57.2 [s, ^1J(PtP) = 3450, P].

Similarly were prepared the following complexes. R = 3,5-$F_2C_6H_3$: yield 80%. Anal. Calcd for $C_{29}H_{14}F_{14}O_4P_2Pt$: C, 36.69; H, 1.49. Found: C, 36.83; H, 1.51. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.84−7.70 [m, 8H, aryl], 7.39 [tt, 4H, ^4J(HH) = 2 Hz, ^3J(FH) = 9 Hz, aryl], 5.36 [t, 2H, ^2J(PH) = 12 Hz, ^3J(PtH) = 91 Hz, $C\boldsymbol{H_2}P_2$]; $\delta(^{31}P)$ = −56.8 [s, ^1J(PtP)=3450, P]. R = 4-MeC_6H_4: yield 60%. Anal. Calcd for $C_{33}H_{30}F_6O_4P_2Pt$: C, 46.0; H, 3.5. Found: C, 45.7; H, 3.7. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.33, 7.82 [m, 16H, aryl], 4.84 [t, 2H, ^2J(PH) = 11 Hz, ^3J(PtH) = 85 Hz, $C\boldsymbol{H_2}P_2$], 2.37 [s, 12H, Me]; $\delta(^{31}P)$ = −70.2 [s, ^1J(PtP) = 3319 Hz, P]. R = 3-MeC_6H_4: yield 98%. Anal. Calcd for $C_{33}H_{30}F_6O_4P_2Pt$: C, 46.0; H, 3.5. Found: C, 45.75; H, 3.7. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.41−7.78 [m, 16H, aryl], 4.94 [t, 2H, ^2J(PH) = 12 Hz, ^3J(PtH) = 87 Hz, $C\boldsymbol{H_2}P_2$], 2.31 [s, 12H, Me]; $\delta(^{31}P)$ = −68.3 [s, ^1J(PtP) = 3324 Hz, P]. R = 2-MeC_6H_4: yield 86%. Anal. Calcd for $C_{33}H_{30}F_6O_4P_2Pt$: C, 46.0; H, 3.5. Found: C, 46.5; H, 3.5. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.32−8.12 [m, 16H, aryl], 5.31 [t, 2H, ^2J(PH) = 11 Hz, ^3J(PtH) = 80 Hz, $C\boldsymbol{H_2}P_2$], 2.28 [s, 12H, Me]; $\delta(^{31}P)$ = −71.4 [s, ^1J(PtP) = 3304 Hz, P]. R = 3,5-$Me_2C_6H_3$: yield 49%. Anal. Calcd for $C_{37}H_{38}F_6O_4P_2Pt$: C, 48.4; H, 4.2. Found: C, 48.7; H, 4.6. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.23 [s, 4H, aryl], 7.55 [m, 8H, aryl], 4.85 [t, 2H, ^2J(PH) = 11 Hz, ^3J(PtH) = 88 Hz, $C\boldsymbol{H_2}P_2$], 2.28 [s, 24H, Me]; $\delta(^{31}P)$ = −68.6 [s, ^1J(PtP) = 3319 Hz, P]. R = 2,4,6-$Me_3C_6H_2$: yield 80%. Anal. Calcd for $C_{41}H_{46}F_6O_4P_2Pt$: C, 50.6; H, 4.8. Found: C, 51.0; H, 4.8. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 6.80 [s, 8H, aryl], 5.26 [t, 2H, ^2J(PH) =

(16) Hietkamp, S.; Sommer, H.; Stelzer, O. *Inorg. Synth.* **1989**, *25*, 120.

11 Hz, ^3J(PtH) = 60 Hz, C$\boldsymbol{H}_2P_2$], 2.24 [s, 12H, Me], 2.35 [s, 24H, Me]; $\delta(^{31}P) = -92.2$ [s, ^1J(PtP) = 3270 Hz, P].

[Pt$_3$(μ_3-CO)(μ-R$_2$PCH$_2$PR$_2$)$_3$(O$_2$CCF$_3$)](O$_2$CCF$_3$). A mixture of [Pt(O$_2$CCF$_3$)$_2$(R$_2$PCH$_2$PR$_2$)], R = 3,5-Cl$_2$C$_6$H$_3$ (1.00 g, 0.93 mmol), MeOH (40 mL), distilled H$_2$O (4 mL), and CF$_3$CO$_2$H (1 mL) in a Parr pressure reactor (300 mL) was heated at 70 °C for 3 days under CO (14 atm). At 12 h intervals for the first 24 h and then 24 h intervals for the remaining 48 h, the pressure reactor was cooled and a fresh CO atmosphere was introduced. After this period, the reactor was cooled to room temperature and opened. The solution was filtered, and the resulting red filtrate was evaporated under vacuum. The orange residue was recrystallized from CH$_2$Cl$_2$/diethyl ether to give the product as an orange solid. Yield: 85%. Anal. Calcd for C$_{80}$H$_{42}$F$_6$O$_5$P$_6$Cl$_{24}$Pt$_3$: C, 34.08; H, 1.50. Found: C, 33.98; H, 1.66. IR (Nujol): ν(CO) = 1771 (s) cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.1−7.6 [m, 36H, C$_6\boldsymbol{H}_3$], 6.6 [d, 3H, ^2J(HH) = 16, CH$^a\boldsymbol{H}^b$], 5.7 [d, 3H, ^2J(HH) = 16, C$\boldsymbol{H}^a$H^b]; $\delta(^{31}P) = -8.4$ [s, ^1J(PtP) = 3673 Hz, ^2J(PtP) = −5 Hz, ^3J(PP) = 169 Hz]; $\delta(^{31}P)$ at −60 °C = −10.3 [br, ^1J(PtP) = 3624]; $\delta(^1H)$ at =90 °C = 5.72 [m, CH$^a\boldsymbol{H}^b$], 4.80 [m, C$\boldsymbol{H}^a\boldsymbol{H}^b$]; $\delta(^{31}P)$ at −90 °C = −4.6 [s, 2P^b, ^1J(PtP) = 3628 Hz, ^3J(P^{b}P$^{b'}$) = 144 Hz], −10.6 [d, 2P^a, ^1J(PtP) = 3616 Hz, ^3J(P^{a}P^c) = 160 Hz], −13.2 [d, 2P^c, ^1J(PtP) = 3746 Hz, ^3J(P^{a}P^c) = 160 Hz]. NMR of ^{13}CO exchanged **1a** at 20 °C in (CD$_3$)$_2$CO: $\delta(^{31}P) = -8.5$ [d, ^1J(PtP) = 3676 Hz, ^2J(PtP) = 2 Hz, ^3J(PP) = 164 Hz, ^2J(CP) = 20 Hz]; $\delta(^{13}C)$ = 188.8 [quintet, ^1J(PtC) = 945 Hz, ^2J(PC) = 20 Hz, Pt*CO*], 52.1 [br, *CH*$_2$P$_2$].

Similarly were prepared the following complexes. R = 3,5-F$_2$C$_6$H$_3$: yield 80%. Anal. Calcd for C$_{80}$H$_{42}$F$_{30}$O$_5$P$_6$Pt$_3$: C, 39.64; H, 1.75. Found: C, 39.52; H, 1.78. IR (Nujol): ν(CO) = 1783(s) cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.4−6.9 [m, C$_6\boldsymbol{H}_3$], 6.7 [d, ^2J(HH) = 13.3 Hz, CH$^a\boldsymbol{H}^b$], 5.7 [d, ^2J(HH) = 13.3 Hz, C$\boldsymbol{H}^a\boldsymbol{H}^b$]; $\delta(^{31}P) = -7.1$ [s, ^1J(PtP) = 3706 Hz, ^2J(PtP) = 13 Hz, ^3J(PP) = 161 Hz]. R = 4-MeC$_6$H$_4$: yield 83%. Anal. Calcd for C$_{92}$H$_{90}$F$_6$O$_5$P$_6$Pt$_3$: C, 51.1; H, 4.2. Found: C, 50.5; H, 4.5. IR (Nujol): ν(CO) = 1740 (s) cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.2−6.7 [m, C$_6\boldsymbol{H}_4$], 5.8 [d, ^2J(HH) = 14 Hz, CH$^a\boldsymbol{H}^b$], 5.6 [d, ^2J(HH) = 14 Hz, C$\boldsymbol{H}^a$H^b]; $\delta(^{31}P) = -11.1$ [s, ^1J(PtP) = 3753 Hz, ^2J(PtP) = 1 Hz, ^3J(PP) = 155 Hz]. R = 3-MeC$_6$H$_4$: yield 98%. Anal. Calcd For C$_{92}$H$_{90}$F$_6$O$_5$P$_6$Pt$_3$: C, 51.1; H, 4.2. Found: C, 51.3; H, 4.7. IR (Nujol): ν(CO) = 1734 (s) cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.3−6.9 [m, C$_6\boldsymbol{H}_4$], 5.63 [d, ^2J(HH) = 13 Hz, CH$^a\boldsymbol{H}^b$], 5.71 [d, ^2J(HH) = 13 Hz, C$\boldsymbol{H}^a$H^b]; $\delta(^{31}P) = -11.2$ [s, ^1J(PtP) = 3741 Hz, ^2J(PtP) = −2 Hz, ^3J(PP) = 157 Hz]. R = 3,5-Me$_2$C$_6$H$_3$: yield 98%. Anal. Calcd for C$_{104}$H$_{114}$F$_6$O$_5$P$_6$Pt$_3$: C, 53.6; H, 4.9. Found: C, 53.3; H, 4.7. IR (Nujol): ν(CO) = 1742 (s) cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.1−6.9 [m, C$_6\boldsymbol{H}_3$], 5.53 [d, ^2J(HH) = 12 Hz, CH$^a\boldsymbol{H}^b$], 5.27 [d, ^2J(HH) = 12 Hz, C$\boldsymbol{H}^a$H^b]; $\delta(^{31}P) = -11.6$ [s, ^1J(PtP) = 3690 Hz, ^2J(PtP) = −3 Hz, ^3J(PP) = 160 Hz].

[Pt$_3$(μ_3-CO)(μ-R$_2$PCH$_2$PR$_2$)$_3$](PF$_6$)$_2$. To a solution of [Pt$_3$(μ_3-CO)(μ-R$_2$PCH$_2$PR$_2$)$_3$(O$_2$CCF$_3$)](O$_2$CCF$_3$), R = 3,5-Cl$_2$C$_6$H$_3$ (0.240 g, 0.085 mmol), in MeOH (5 mL) was added dropwise a filtered solution of NH$_4$PF$_6$ (0.222 g, 1.36 mmol) in MeOH (5 mL). An orange precipitate formed immediately. After 4 h, the product was collected by filtration and washed with MeOH (0.5 mL). Recrystallization from CH$_2$Cl$_2$/ether followed by vacuum drying afforded the orange-red crystalline product in 85% yield. Anal. Calcd for C$_{76}$H$_{42}$Cl$_{24}$F$_{12}$OP$_8$Pt$_3$: C, 31.66; H, 1.47. Found: C, 31.78; H, 1.65. IR (Nujol): ν(CO) = 1771 (s) cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.6−7.1 [m, C$_6\boldsymbol{H}_3$], 6.5 [d, ^2J(HH) = 16 Hz, CH$^a\boldsymbol{H}^b$], 5.6 [d, ^2J(HH) = 16, C$\boldsymbol{H}^a\boldsymbol{H}^b$]; $\delta(^{31}P) = 8.4$ [s, ^1J(PtP) = 3672 Hz, ^2J(PtP) = −3 Hz, ^3J(PP) = 174 Hz]; $\delta(^1H)$ at 90 °C = 5.72 [m, CH$^a\boldsymbol{H}^b$], 4.82 [m, C$\boldsymbol{H}^a\boldsymbol{H}^b$]; $\delta(^{31}P)$ at −90 °C = −4.6 [s, 2P^b, ^1J(PtP) = 3622 Hz, ^3J(P^{b}P$^{b'}$) = 143 Hz], −10.6 [d, 2P^a, ^1J(PtP) = 3606 Hz, ^3J(P^{a}P^c) = 160 Hz], −13.2 [d, 2P^c, ^1J(PtP) = 3746 Hz, ^{3}J(P^{a}P^c) = 160 Hz].

Similarly were prepared the following complexes. R = 3,5-F$_2$C$_6$H$_3$: yield 84%. Anal. Calcd for C$_{76}$H$_{42}$F$_{36}$OP$_8$Pt$_3$: C, 36.69; H, 1.70. Found: C, 36.99; H, 1.86. IR (Nujol): ν(CO) = 1784 (s) cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.4−6.7 [m, C$_6\boldsymbol{H}_3$], 6.4 [d, ^2J(HH) = 14 Hz, CH$^a\boldsymbol{H}^b$], 5.9 [d, ^2J(HH) = 14 Hz, C$\boldsymbol{H}^a\boldsymbol{H}^b$]; $\delta(^{31}P)$ = 0.4 [s, ^1J(PtP) = 3759 Hz, ^2J(PtP) = 32 Hz, ^3J(PP) = 110 Hz]. R = 4-MeC$_6$H$_4$: yield 94%. Anal. Calcd for C$_{88}$H$_{90}$F$_{12}$OP$_8$Pt$_3$: C, 47.51; H, 4.08. Found: C, 47.74; H, 4.52. IR (Nujol): ν(CO) = 1754(s) cm^{-1}, ν(^{13}CO) = 1711 cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.2−6.9 [m, C$_6\boldsymbol{H}_4$], 6.0 [d, ^2J(HH) = 16 Hz, CH$^a\boldsymbol{H}^b$], 5.55 [d, ^2J(HH) = 16 Hz, C$\boldsymbol{H}^a\boldsymbol{H}^b$], 2.26, 2.25 [s, MeC]; $\delta(^{31}P) = -7.39$ [s, ^1J(PtP) = 3706 Hz, ^2J(PtP) = −3 Hz, ^3J(PP) = 138 Hz]; $\delta(^{13}C)$ = 211.1 [br s, ^1J(PtC) = 750 Hz]. R = 3-MeC$_6$H$_4$: yield 99%. Anal. Calcd for C$_{88}$H$_{90}$F$_{12}$OP$_8$Pt$_3$: C, 47.51; H, 4.08. Found: C, 47.24; H, 4.50. IR (Nujol): ν(CO) = 1734 (s) cm^{-1}, ν(^{13}CO) = 1696 cm^{-1}. NMR in CD$_2$Cl$_2$: $\delta(^1H)$ = 7.0−6.8 [m, C$_6\boldsymbol{H}_4$], 5.4 [d, ^2J(HH) = 15 Hz, CH$^a\boldsymbol{H}^b$], 5.3 [d, ^2J(HH) = 15 Hz, C$\boldsymbol{H}^a\boldsymbol{H}^b$], 2.12, 2.00 [s, Me]; $\delta(^{31}P)$ = −6.81 [s, ^1J(PtP) = 3701 Hz, ^3J(PP) = 144 Hz]; $\delta(^{13}C)$ = 209.6 [m, ^1J(PtC) = 806 Hz, ^2J(PC) = 25 Hz]. R = 3,5-Me$_2$C$_6$H$_3$: yield 98%. Anal. Calcd for C$_{100}$H$_{114}$F$_{12}$OP$_8$Pt$_3$: C, 50.19; H, 4.80. Found: C, 50.00; H, 5.08. IR (Nujol): ν(CO) = 1743 (s) cm^{-1}, ν(^{13}CO) = 1703 cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 7.2−6.8 [m, C$_6\boldsymbol{H}_3$], 5.8 [d, ^2J(HH) = 14 Hz, CH$^a\boldsymbol{H}^b$], 5.2 [d, ^2J(HH) = 14 Hz, C$\boldsymbol{H}^a\boldsymbol{H}^b$], 2.14, 1.99 [s, Me]; $\delta(^{31}P) = -5.2$ [s, ^1J(PtP) = 3697 Hz, ^3J(PP) = 139 Hz]; $\delta(^{13}C)$ = 213.4 [m, ^1J(PtC) = 670 Hz]. NMR at −90 °C: $\delta(^{31}P) = -7.8$ [br s, ^1J(PtP) = 3640 Hz]; $\delta(^{13}C)$ = 210.4 [m, ^1J(PtC) = 800 Hz, ^2J(PC) = 18 Hz].

[Pt$_2$H(CO)(μ-R$_2$PCH$_2$PR$_2$](CF$_3$CO$_2$), R = 2-MeC$_6$H$_4$. A mixture of [Pt(O$_2$CCF$_3$)$_2$(R$_2$PCH$_2$PR$_2$)] (0.66 g), MeOH (35 mL), and H$_2$O (3 mL) was heated in a 300 mL pressure reactor with CO (60 psi) for 3 days. Workup in the usual way gave the product as a yellow solid. Yield: 85%. Anal. Calcd for C$_{61}$H$_{61}$F$_3$O$_3$P$_4$Pt$_2$: C, 51.84; H, 4.35. Found: C, 51.47; H, 4.35. IR (Nujol): ν(CO) = 2043 (s) cm^{-1}, ν(^{13}CO) = 1993 cm^{-1}; ν(PtH) = 2074 cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = 8.6−6.0 [m, C$_6\boldsymbol{H}_4$], 4.3 [m, CH$_2$P$_2$], 2.00, 1.99 [s, Me], −6.77 [m, ^{1}J(PtH) = 990 Hz, ^{2}J(PtH) = 120 Hz, ^{2}J(PH) = 20 Hz, PtH]; $\delta(^{31}P)$ = 2.61 [m, ^1J(PtP) = 2720 Hz, PtP^a], 7.66 [m, ^1J(PtP) = 3385 Hz, PtP^b]; $\delta(^{13}C)$ = 189.1 [m, ^1J(PtC) = 1138 Hz, ^2J(PtC) = 195 Hz, ^2J(PC) = 7 Hz, CO]. NMR at −90 °C: $\delta(^{31}P) = -7.8$ [br s, ^1J(PtP) = 3640 Hz]; $\delta(^{13}C)$ = 210.4 [m, ^1J(PtC) = 800 Hz, ^2J(PC) = 18 Hz].

[Pt$_2$H$_2$(μ-H)(μ-R$_2$PCH$_2$PR$_2$)$_2$](PF$_6$), R = 2-MeC$_6$H$_4$. To a stirred suspension of [PtCl$_2$(R$_2$PCH$_2$PR$_2$)] (0.5 g) in MeOH (50 mL) was added a solution of Na[BH$_4$] (0.35 g) in EtOH (30 mL). After 4 h, the mixture was filtered, NH$_4$[PF$_6$] (0.84 g) was added to the filtrate, and the solvent was evaporated. The residue was extracted with CH$_2$Cl$_2$ (10 mL), and the product was obtained by precipitation with pentane (20 mL). Yield: 76%. Anal. Calcd for C$_{58}$H$_{63}$F$_6$P$_5$Pt$_2$: C, 49.09; H, 4.47. Found: C, 49.12; H, 4.53. IR (Nujol): ν(PtH) = 2130 cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = −7.42 [t, ^1J(PtH) = 1170 Hz, ^2J(PtH) = 105 Hz, ^2J(PH) = 7 Hz, PtH^t], −6.06 [m, ^1J(PtH) = 570 Hz, PtH^b], 2.06 [s, Me], 5.05 [m, ^{3}J(PtH) = 37 Hz, ^{4}J(PH) = 4 Hz, CH$_2$P$_2$]; $\delta(^{31}P)$ = 9.04 [s, ^1J(PtP) = 2692 Hz, dppm]. Similarly was prepared the corresponding trideuteride derivative by using NaBD$_4$; ν(PtD) = 1530 cm^{-1}. Similarly was prepared the complex with R = 3,5-Me$_2$C$_6$H$_3$. Yield: 58%. Anal. Calcd for C$_{66}$H$_{79}$F$_6$P$_5$Pt$_2$: C, 51.76; H, 5.20. Found: C, 51.05; H, 5.06. IR (Nujol): ν(PtH) = 2105 cm^{-1}. NMR in (CD$_3$)$_2$CO: $\delta(^1H)$ = −6.81 [dt, ^1J(PtH) = 1132 Hz, ^2J(PtH) = 106 Hz, ^2J(PH) = 6 Hz, ^2J(H^{b}H^t) = 15 Hz, PtH^t], −6.10 [m, ^1J(PtH) = 544 Hz, PtH^b], 2.24 [s, Me], 4.51 [m, ^3J(PtH) = 34 Hz, CH$_2$P$_2$]; $\delta(^{31}P)$ = 19.63 [s, ^{1}J(PtP) = 2758 Hz, ^{3}J(PtP) = 10 Hz, ^2J(PP) = −29, 76 Hz, dppm].

[Pt$_4$(μ_2-CO)$_2$(μ_2-H)(R$_2$PCH$_2$PR$_2$)$_4$][PF$_6$], R = 3,5-F$_2$C$_6$H$_3$. A mixture of [Pt(R$_2$PCH$_2$PR$_2$)(O$_2$CCF$_3$)$_2$], R = 3,5-F$_2$C$_6$H$_3$ (1.00 g, 1.05 mmol), MeOH (40 mL), and triple distilled H$_2$O (4 mL) in a Parr pressure reactor (300 mL) was heated at 65 °C for 4 d under CO (20 atm). At 12 h intervals for the first 24 h and then at 24 h intervals for the remaining 72 h, a fresh CO atmosphere was introduced. The reactor was cooled to room temperature and opened. The reddish solution was filtered, and the filtrate was evaporated to dryness under vacuum. The red residue was dissolved in MeOH (5 mL), and to this solution was added dropwise a prefiltered solution of NH$_4$PF$_6$ (1.40 g, 8.59 mmol) in MeOH (5 mL). After 4 h, the solution was

filtered and the filtrate was evaporated to dryness. The residue was then extracted with CH_2Cl_2, and the product was isolated by evaporation of the solvent as a red crystalline product. Yield: 82%. Anal. Calcd for $C_{102}H_{55}F_{38}O_2P_9Pt_4$: C, 39.57; H, 1.86. Found: C, 39.85; H, 1.92%. IR (Nujol): ν(CO) = 1824 (s), 1784 (s) cm^{-1}. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 4.26 [d, 3H, ^2J(HH) = 13 Hz, ^3J(PtH) = 25 Hz, CH^a***H***^{b} of μ-PP], 4.24 [d, 3H, ^2J(HH) = 13 Hz, ^3J(PtH) = 25 Hz, C***H***^{a}***H***^{b} of μ-PP], 3.66 [d, 2H, ^2J(PH) = 11 Hz, ^3J(PtH) = 62 Hz, C***H***$_2$ of ^{n1}-PP], −7.2 [quin, 1H, ^1J(PtH) = 532 Hz, ^2J(PtH) = 32 Hz, ***H***Pt$_2$]; $\delta(^{31}P)$ = −22.6 [s, 1P, ^1J(PtP) = 4520 Hz, ^2J(PtP) = 166 Hz], −12.5 [s, 6P, ^1J(PtP) = 3271 Hz, ^2J(PtP) = 206 Hz, ^3J(PP) = 200 Hz], −21.9 [d, 1P, ^3J(PtP) = 80 Hz].

Similarly were prepared the following complexes. R = 4-MeC_6H_4: yield 45%. Anal. Calcd for $C_{118}H_{121}F_6O_2P_9Pt_4$: C, 51.64; H, 4.44. Found: C, 51.77; H, 5.06. IR (Nujol): ν(CO) = 1800 (s), 1757 (s) cm^{-1}, $\nu(^{13}CO)$ = 1760 (s), 1725 (s) cm^{-1}. NMR in $(CD_3)_2CO$ at −40 °C: $\delta(^1H)$ = 4.82, 4.78, 3.93, 3.87 [m, CH^a***H***^{b} of μ-PP], 3.45 [d, 2H, ^2J(PH) = 10 Hz, ^3J(PtH) = 50 Hz, C***H***$_2$ of μ-PP], −7.9 [m, 1H, ^1J(PtH) = 672 Hz, ^2J(PtH) = 175 Hz, ***H***Pt$_2$]; $\delta(^{13}C)$ = 247.8 [m, ^1J(PtC) = 821 Hz, 403 Hz, ^2J(PC) = 19, ^{13}CO]; $\delta(^{31}P)$ = −24.9 [m, 1P, ^1J(PtP) = 4520 Hz, ^2J(PtP) = 166 Hz], −12.5 [s, 6P, ^1J(PtP) = 3271 Hz, ^2J(PtP) = 206 Hz, ^3J(PP) = 200 Hz], −21.9 [d, 1P, ^3J(PtP) = 80 Hz].

$Pt_3(\mu_3\text{-CO})(\mu_3\text{-I})(\mu\text{-R}_2PCH_2PR_2)_3][PF_6]$, R = 3,5-$Cl_2C_6H_3$. To a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3](PF_6)_2$ (40 mg, 0.014 mmol) in acetone (10 mL) was added MeI (0.20 mL, 3.21 mmol) via microsyringe. The orange solution darkened immediately. After 4 h, NH_4PF_6 (10 mg) was added, the solution was stirred for another 10 min, and the solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (10 mL), and the solvent was removed under vacuum to give the product as an organge solid, which was recrystallized from acetone/*n*-pentane. Yield: 94%. Anal. Calcd for $C_{76}H_{42}Cl_{24}F_6IOP_7Pt_3$: C, 31.86; H, 1.48. Found: C, 31.74; H, 1.63. IR (Nujol): ν(CO) = 1785 (s) cm^{-1}. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.6−7.3 [m, C$_6$***H***$_3$], 6.6 [d, ^2J(HH) = 14 Hz, CH^a***H***^{b}], 5.6 [d, ^2J(HH) = 14 Hz, C***H***^{a}H^b]; $\delta(^{31}P)$ = −10.1 [s, ^1J(PtP) = 3989 Hz, ^2J(PtP) = 55 Hz, ^3J(PP) = 131 Hz].

Similarly were prepared the following complexes. R = 3,5-$F_2C_6H_3$: yield 89%. Anal. Calcd for $C_{76}H_{42}F_{30}IOP_7Pt_3$: C, 36.96; H, 1.71. Found: C, 36.99; H, 1.80. IR (Nujol): ν(CO) = 1788(s) cm^{-1}. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.2−7.1 [m, C$_6$***H***$_3$], 6.6 [d, ^2J(HH) = 13.8 Hz, CH^a***H***^{b}], 5.9 [d, ^2J(HH) = 13.8 Hz, C***H***^{a}H^b]; $\delta(^{31}P)$ = −8.5 [s, ^1J(PtP) = 3961 Hz, ^2J(PtP) = 28 Hz, ^3J(PP) = 168 Hz, dppm]. R = 4-MeC_6H_4: yield 93%. Anal. Calcd for $C_{88}H_{90}F_6IOP_7Pt_3{\cdot}2Me_2CO$: C, 48.61; H, 4.43. Found: C, 48.89; H, 4.91. IR (Nujol): ν(CO) = 1757 (s) cm^{-1}. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.2−6.9 [m, C$_6$***H***$_4$], 5.77 [d, ^2J(HH) = 13 Hz, CH^a***H***^{b}], 5.23 [d, ^2J(HH) = 13 Hz, C***H***^{a}H^b], 2.20, 2.23 [s, Me]; $\delta(^{31}P)$ = −16.1 [s, ^1J(PtP) = 3902 Hz, ^2J(PtP) = −28 Hz, ^3J(PP) = 160 Hz, dppm]. R = 3-MeC_6H_4: yield 75%. Anal. Calcd for $C_{88}H_{90}F_6IOP_7Pt_3{\cdot}2Me_2CO$: C, 48.61; H, 4.43. Found: C, 48.20; H, 4.23. IR (Nujol): ν(CO) = 1757 (s) cm^{-1}. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.2−6.95 [m, C$_6$***H***$_4$], 5.81 [d, ^2J(HH) = 14 Hz, CH^a***H***^{b}], 5.36 [d, ^2J(HH) = 14 Hz, C***H***^{a}H^b], 2.09, 2.03 [s, Me]; $\delta(^{31}P)$ = −15.4 [s, ^1J(PtP) = 3889 Hz, ^2J(PtP) = −30 Hz, ^3J(PP) = 162 Hz, dppm]. R = 3,5-$Me_2C_6H_4$: yield 99% from CH_2Cl_2. Anal. Calcd for $C_{100}H_{114}F_6IOP_7Pt_3{\cdot}CH_2Cl_2$: C, 49.32; H, 4.75. Found: C, 49.03; H, 5.19. IR (Nujol): ν(CO) = 1757 (s) cm^{-1}. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.6−6.8 [m, C$_6$***H***$_3$], 5.66 [d, ^2J(HH) = 14 Hz, CH^a***H***^{b}], 5.20 [d, ^2J(HH) = 14 Hz, C***H***^{a}H^b], 2.03, 1.98 [s, Me]; $\delta(^{31}P)$ = −16.0 [s, ^1J(PtP) = 3893 Hz, ^2J(PtP) = −27 Hz, ^3J(PP) = 162 Hz, dppm].

$[Pt_3(\mu_3\text{-CO})(SCN)(\mu\text{-R}_2PCH_2PR_2)_3][PF_6]$, R = 3,5-$Cl_2C_6H_3$. To a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3](PF_6)_2$ (50 mg, 0.017 mmol) in acetone (10 mL) was added KSCN (8.4 mg, 0.087 mmol). An immediate color change to orange-red occurred. The mixture was stirred for 4 h and then NH_4PF_6 (10 mg) was added and stirred for another 10 min. The solvent was evaporated under vacuum, the residue was extracted with CH_2Cl_2 (15 mL), and the CH_2Cl_2 was evaporated to give the product as a red solid which was recrystallized from acetone/*n*-pentane. Yield: 92%. Anal. Calcd for $C_{77}H_{42}Cl_{24}F_6NOP_7Pt_3S$: C, 33.08; H, 1.51. Found: C, 33.48; H, 1.72. IR (Nujol): ν(CN) = 2089 (s), 2065 (sh), ν(CO) = 1786 (s) cm^{-1}. NMR in $(CD_3)CO$: $\delta(^1H)$ = 7.6−7.3 [m, C$_6$***H***$_3$], 6.6 [d, ^2J(HH) = 12.5 Hz, CH^a***H***^{b}], 5.9 [d, ^2J(HH) = 12.5 Hz, C***H***^{a}H^b]; $\delta(^{31}P)$ = −10.4 [s, ^1J(PtP) = 3670 Hz, ^2J(PtP) = 9 Hz, ^3J(PP) = 164 Hz, dppm].

Similarly were prepared the following complexes. R = 3,5-$F_2C_6H_3$: yield 90%. Anal. Calcd for $C_{77}H_{42}F_{30}NOP_7Pt_3S$: C, 38.51; H, 1.76. Found: C, 38.97; H, 1.85. IR (Nujol): ν(CN) = 2083 (sh), 2053 (s), ν(CO) = 1782 (s) cm^{-1}. NMR in $(CD_3)_2$-CO: $\delta(^1H)$ = 7.3−7.0 [m, C$_6$***H***$_3$], 6.5 [d, ^2J(HH) = 13.9 Hz, CH^a***H***^{b}], 5.9 [d, ^2J(HH) = 13.9 Hz, C***H***^{a}H^b]; $\delta(^{31}P)$ = −10.5 [s, ^1J(PtP) = 3691 Hz, ^2J(PtP) = 4 Hz, ^3J(PP) = 168 Hz, dppm]. R = 3,5-$Me_2C_6H_3$: yield 93%. Anal. Calcd for $C_{102}H_{114}F_6NOP_7Pt_3S$: C, 52.60; H, 4.98. Found: C, 52.11; H, 5.15. IR (Nujol): ν(CN) = 2080 (sh), 2053 (s), ν(CO) = 1752 (s) cm^{-1}. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.6−6.8 [m, C$_6$***H***$_3$], 5.49 [d, ^2J(HH) = 12 Hz, CH^a***H***^{b}], 5.35 [d, ^2J(HH) = 12 Hz, C***H***^{a}H^b], 2.02, 1.98 [s, Me]; $\delta(^{31}P)$ = −16.0 [s, ^1J(PtP) = 3656 Hz, ^2J(PtP) = −1 Hz, ^3J(PP) = 166 Hz, dppm].

$Pt_3(\mu_3\text{-CO})(P(OPh)_3)(\mu\text{-R}_2PCH_2PR_2)_3][PF_6]_2$, R = 3,5-$F_2C_6H_3$. To a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3][PF_6]_2$, R = 3,5-$F_2C_6H_3$ (38 mg, 0.015 mmol), in $(CD_3)_2CO$ (0.5 mL) in an NMR tube was added $P(OPh)_3$ (0.8 μL, 0.030 mmol) via microsyringe at −78 °C. Upon mixing, the solution changed from orange to orange red. The product was characterized spectroscopically at temperatures below −40 °C. At temperatures from 0 to 25 °C, only starting materials were observed in solution by NMR. NMR spectra in $(CD_3)_2CO$ at −90 °C: $\delta(^1H)$ = 5.80 [m, CH^a***H***^{b}], 5.20 [m, C***H***^{a}H^b]; $\delta(^{31}P)$ = 88.8 [t, 1P^x, ^1J(PtP) = 5362 Hz, ^2J(PtP) = 525 Hz], δ = −0.03 [s, 2P^b, ^1J(PtP) = 3142 Hz, ^3J(P^{b}P$^{b'}$) = 154 Hz], −2.8 [d, 2P^a, ^1J(PtP) = 3896 Hz, ^3J(P^{a}P^c) = 177 Hz], −28.4 [d, 2P^c, ^1J(PtP) = 2520 Hz, ^3J(P^{a}P^c) = 177 Hz]. NMR at −60 °C: $\delta(^1H)$ = 5.84 [m, CH^a***H***^{b}], 5.20 [m, C***H***^{a}H^b]; $\delta(^{31}P)$ = 88.8 [t, 1P^x, ^1J(PtP) = 5362 Hz, ^2J(PtP) = 525 Hz], −0.15 [s, 2P^b, ^1J(PtP) = 3126 Hz, ^3J(P^{b}P$^{b'}$) = 145 Hz], −2.9 [d, 2P^a, ^1J(PtP) = 3894 Hz, ^3J(P^{a}P^c) = 177 Hz], −28.8[d, 2P^c, ^1J(PtP) = 2520 Hz, ^3J(P^{a}P^c) = 177 Hz].

Reaction of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3](PF_6)_2$, R = 3,5-$Cl_2C_6H_3$, with $P(OPh)_3$. The same procedure as above was applied to the reaction of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3](PF_6)_2$, R = 3,5-$Cl_2C_6H_3$, with $P(OPh)_3$. $^{31}P\{^1H\}$ NMR results showed only the existence of starting materials at temperatures between −90 to 20 °C.

Reactions with $P(Ph)_3$. Reaction of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3](PF_6)_2$, R = 3,5-$F_2C_6H_3$ or 3,5-$Cl_2C_6H_3$, with PPh_3 was studied as above. No reaction was detected at temperatures between −90 and 20 °C according to NMR measurements.

$[Pt_3(\mu_3\text{-CO})(P(OMe)_3)(\mu\text{-R}_2PCH_2PR_2)_3][O_2CCF_3]_2$, R = 3,5-$Cl_2C_6H_3$. To a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3][O_2CCF_3]_2$, R = 3,5-$Cl_2C_6H_3$ (22 mg, 0.008 mmol), in $(CD_3)_2CO$ (0.5 mL) in an NMR tube was added $P(OMe)_3$ (0.95 μL, 0.008 mmol) via microsyringe at −78 °C. Upon mixing, the solution changed from organge yellow to orange red. The product was characterized spectroscopically at temperatures below 60 °C. NMR spectra in $(CD_3)_2CO$ at −90 °C: $\delta(^1H)$ = 5.62 [br, CH^a***H***^{b}], 5.00 [br, C***H***^{a}H^b], 3.95 [m, P(OC***H***$_3$)$_3$]; $\delta(^{31}P)$ = 100.9 [t, 1P^x, ^1J(PtP) = 4900 Hz, ^2J(PtP) = 460 Hz], −1.1 [s, 2P^b, ^1J(PtP) = 3106 Hz, ^3J(P^{b}P$^{b'}$) = 135 Hz], −3.8 [d, 2P^a, ^1J(PtP) = 3929 Hz, ^3J(P^{a}P^c) = 172 Hz], −28.5 [d, 2P^c, ^1J(PtP) = 2503 Hz, ^3J(P^{a}P^c) = 172 Hz]. NMR at −60 °C: $\delta(^1H)$ = 5.58 [br, CH^a***H***^{b}], 5.04 [br, C***H***^{a}H^b], 4.00 [m, P(OC***H***$_3$)$_3$]; $\delta(^{31}P)$ = 100.7 [t, 1P^x, ^1J(PtP) = 4938 Hz, ^2J(PtP) = 452 Hz], −1.6 [s, 2P^b, ^1J(PtP) = 3070 Hz, ^3J(P^{b}P$^{b'}$) = 129 Hz], −3.6 [d, 2P^a, ^1J(PtP) = 3946 Hz, ^3J(P^{a}P^c) = 174 Hz], −28.7 [d, 2P^c, ^1J(PtP) = 2482 Hz, ^3J(P^{a}P^c) = 174 Hz].

Similarly, $[Pt_3(\mu_3\text{-CO})(P(OMe)_3)(\mu\text{-R}_2PCH_2PR_2)_3][PF_6]_2$, R = 3,5-$F_2C_6H_3$, was prepared in solution by reaction of $[Pt_3(\mu_3\text{-CO})(\mu\text{-R}_2PCH_2PR_2)_3][PF_6]_2$, R = 3,5-$F_2C_6H_3$ (20 mg, 0.008 mmol), with $P(Ome)_3$ (0.95 μL, 0.008 mmol) at −78 °C. Compound **6b** was characterized spectroscopically at temper-

Table 5. Crystal Data and Experimental Details for the Compound $[Pt_3(R_2PCH_2PR_2)_3(\mu_3\text{-}CO)(O_2CCF_3)](CF_3CO_2)\cdot 0.5CH_2Cl_2\cdot 1.5H_2O$, R = 3,5-$Cl_2C_6H_3$, 4e

formula	$C_{80}H_{42}Cl_{24}F_6O_5P_6Pt_3\cdot 0.5CH_2Cl_2\cdot 1.5H_2O$
fw	2888.64
cryst system, space group	monoclinic, $P2_1/n$
cell dimens	a = 23.365(4) Å b = 24.599(4) Å c = 19.141(7) Å β = 102.44(2)°
cell vol (Å^3), Z	10743(5), 4
density (g·cm^{-3}): obsd, calcd	1.76(5), 1.786
radiation, wavelength (Å)	Mo Kα, 0.710 73
abs coeff (cm^{-1})	44.5
R^a	0.0727

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

atures below 40 °C. NMR in $(CD_3)_2CO$ at −90 °C: $\delta(^1H)$ = 6.28 [br, CH^aH^b], 5.02 [br, CH^aH^b], 3.90 [m, $P(OCH_3)_3$]; $\delta(^{31}P)$ = 101.7 [t, $1P^x$, $^1J(PtP)$ = 4951 Hz, $^2J(PtP)$ = 414 Hz], −1.2 [s, $2P^b$, $^1J(PtP)$ = 3174 Hz, $^3J(P^bP^{b'})$ = 161], −3.1 [d, $2P^a$, $^1J(PtP)$ = 4032 Hz, $^3J(P^aP^c)$ = 168 Hz], −26.8 [d, $2P^c$, $^1J(PtP)$ = 2639 Hz, $^3J(P^aP^c)$ = 168 Hz]. NMR at −60 °C: $\delta(^1H)$ = 6.27 [br, CH^aH^b], 5.01 [m, CH^aH^b], 3.93 [m, $P(OCH_3)_3$]; $\delta(^{31}P)$ = 101.3 [t, $1P^x$, $^1J(PtP)$ = 4923 Hz, $^2J(PtP)$ = 424 Hz], −1.0 [s, $2P^b$, $^1J(PtP)$ = 3142 Hz, $^3J(P^bP^{b'})$ = 149 Hz], −2.9 [d, $2P^a$, $^1J(PtP)$ = 4050 Hz, $^3J(P^aP^c)$ = 169 Hz], −27.0 [d, $2P^c$, $^1J(PtP)$ = 2638 Hz, $^3J(P^aP^c)$ = 169 Hz]. ^{31}P NMR measurement at ambient temperature showed two broad peaks at −3 and −28 ppm. The product could not be isolated as a pure solid due to its thermal instability.

Similarly addition of $PMePh_2$ gave the following adducts. R = 3,5-$Me_2C_6H_3$: NMR in CD_2Cl_2 at −80 °C $\delta(^{31}P)$ = −12.4 [t, $1P^x$, $^JJ(PtP)$ = 2880 Hz], −15.9 [s, $2P^b$, $^1J(PtP)$ = 3300 Hz, $^3J(P^bP^{b'})$ = 140], −45.4 [d, $2P^a$, $^1J(PtP)$ = 2620 Hz, $^3J(P^aP^c)$ = 180 Hz], −15.5 [d, $2P^c$, $^1J(PtP)$ = 3720 Hz, $^3J(P^aP^c)$ = 180 Hz]. R = 3-MeC_6H_4; NMR in CD_2Cl_2 at −80 °C $\delta(^{31}P)$ = −9.1 [t, 1P, $^1J(PtP)$ = 2700 Hz, $PMePh_2$], −15.0 [s, $2P^b$, $^1J(PtP)$ = 3300 Hz, $^3J(P^bP^{b'})$ = 140], −43.0 [d, $2P^a$, $^1J(PtP)$ = 2670 Hz, $^3J(P^aP^c)$ = 180 Hz], −15.1 [d, $2P^c$, $^1J(PtP)$ = 3760 Hz, $^3J(P^aP^c)$ = 180 Hz]. R = 4-MeC_6H_4: NMR in CD_2Cl_2 at −80 °C $\delta(^{31}P)$ = −21.9 [t, 1P, $^1J(PtP)$ = 2720 Hz, $PMePh_2$], −13.6 [s, $2P^b$, $^1J(PtP)$ = 3200 Hz, $^3J(P^bP^{b'})$ = 150 Hz], −40.1 [d, $2P^a$, $^1J(PtP)$ = 2600 Hz, $^3J(P^aP^c)$ = 185 Hz], −14.2 [d, $2P^c$, $^1J(PtP)$ = 3800 Hz, $^3J(P^aP^c)$ = 185 Hz].

X-ray Crystallography. Orange-yellow, rodlike crystals of **4e**(CF_3CO_2) were grown with difficulty from CH_2Cl_2/Et_2O. Data were collected at −50 °C, since solvent loss and crystal decay occurred at room temperature, by using an Enraf-Nonius CAD4F diffractometer[17] with graphite-monochromated Mo Kα radiation. Photo and automatic indexing routines, followed by least-squares fits of 21 accurately centered reflections (24.5 ≤ 2θ ≤ 31.3°), gave cell constants and an orientation matrix. The Niggli matrix suggested the monoclinic system with symmetry 2/m, and this was confirmed from an inspection of equivalent reflections. Intensity data were recorded in ω−2θ mode, at variable scan speeds (2.06−4.12 deg·min^{-1}) and a scan width of 1.0 + 0.35 tan θ, with a maximum time per datum of 45 s. Background measurements were made by extending the scan by 25% on each side. Three standard reflections were monitored every 120 min of X-ray exposure time, and orientation checks were done for every 250 reflections measured. There were 15 859 reflections in the 2θ range 0−45° (−25 ≤ h ≤ 25, −26 ≤ k ≤ 1, −20 ≤ l ≤ 1), and 90 repetitions of the standards were recorded. Corrections were made for Lorentz, monochromator and crystal polarization, background radiation effects, and decay using the NRCVAX crystal structure programs[18] running on a SUN 3/80 workstation. The data crystal had six faces which were indexed, and the distances between them were measured for absorption (μ = 44.5 cm^{-1}). A Gaussian absorption correction was applied using the program "ABSO"; the maximum and minimum transmission values were 0.5266 and 0.4256. There were 14 042 independent reflections of which 6792 were considered observed (for $I \geq 2.5\sigma(I)$). The systematic absences[19] indicated that the space group was $P2_1/n$, and the correctness of the choice of the space group was confirmed by successful solution and refinement of the structure. The positions of the heavy atoms were determined by using the program SHELXS-86,[20] and the remaining atoms were located by subsequent difference Fourier techniques. Initial least-squares refinements were performed using SHELX-76,[21] and final full-matrix least-squares refinements on F^2 using SHELXL-93.[22] Anisotropic thermal parameters were assigned and refined for all the Pt, P, Cl, and the F atoms in the cation. The phenyl ring carbon atoms were treated as regular hexagons with d(C−C) = 1.390 Å, and their individual isotropic thermal parameters were refined in the least-squares cycles. The hydrogen atoms were placed in ideal calculated positions (d(C−H) = 0.97 and 0.93 Å for methylene and phenyl groups, respectively). Of the two trifluoroacetate groups one was found to be a part of the cation. Two fragments of the other trifluoroacetate anion were successfully located, and their occupancy factors were refined to 0.55 and 0.45. The trifluoroacetate groups were constrained to have equivalent C−F, C−C, and C−O bonds of equal length. A common isotropic thermal parameter was refined for the F atoms and for the CCO_2 group. A half-molecule of disordered dichloromethane was located, and the occupancy factors were assigned by comparing with the electron densities of other peaks in the difference Fourier. Three peaks found in the electron density maps were assigned as oxygen atoms of water molecules. No hydrogen atoms were included for these solvent molecules. The model converged to R = 0.0727 for 6958 data with $F_o > 4\sigma(F_o)$. The maximum shift = 0.037 Å for C(11) and the maximum dU = 0.012 for F(3). Tables of crystal data, positional and thermal parameters, anisotropic thermal parameters, hydrogen atom positional parameters, selected weighted least-squares planes, and dihedral angles have been included in the depository materials.

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Supplementary Material Available: Tables of crystallographic experimental details, fractional coordinates and B_{iso} values, bond distances and angles, anisotropic thermal parameters, hydrogen coordinates, and least-squares planes and dihedral angles (15 pages). Ordering information is given on any current masthead page.

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