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Carbonylation of Organoplatinum Dimers Bridged by (Diphenylphosphino)cyclopentadienyl Ligands. Structural Characterization of Complexes Containing 1,1- or 1,2-Substituted η^1-Cyclopentadienyl Groups and Reductive Elimination of Ketones

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The complexes [$Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2$] (**1a–e**: R = Me, Et, neo-Pe (CH_2CMe_3), Ph, Bz (CH_2-Ph)) react with carbon monoxide to produce [$Pt_2R_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$] (**2a–e**), in which the cyclopentadienyl groups are 1,2-substituted by Pt and P. The R and CO ligands occupy mutually trans positions, and the complexes exist in solution as both *syn* and *anti* forms. The molecular structures of the methyl and neopentyl derivatives have been determined by X-ray diffraction, and they adopt *anti* and *syn* conformations, respectively. Thermolyses of these complexes in the presence of CO leads to the platinum(I) dimer [$Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$] (**5**), in which both cyclopentadienyl rings are 1,1-substituted, and the appropriate ketone. The molecular structure of **5** reveals a Pt–Pt distance of 2.583(1) Å. Careful monitoring by NMR spectroscopy of the carbonylation/reductive-elimination sequence allows the identification of the intermediates [$Pt_2R(COR)(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$] (**3b,c**) and [$Pt_2R(CO)(COR)(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$] (**4b,c**). The molecular structure of **4c** indicates that the complex contains one 1,1- and one 1,2-substituted cyclopentadienyl moiety and a Pt→Pt dative bond. A mechanism for the carbonylation/reductive-elimination sequence is proposed.

Introduction

A numer of dimeric metal complexes bridged by the (diphenylphosphino)cyclopentadienyl (dppc) ligand have been reported in recent years.[1,2] These include several symmetrical late-transition-metal complexes bridged by dppc or its (dimethylphosphino)cyclopentadienyl (dmpc) analogue.[3–7] In each case, until our own work with diplatinum species,[2] the bridging dppc or dmpc ligand was found to coordinate through phosphorus to one metal center and through the η^5-cyclopentadienyl ring to the other.

We have reported recently that the diplatinum complexes [$Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2$] (**1a–d**: R = Me, Et, neo-Pe (CH_2CMe_3), Ph) exist in solution as a mixture of symmetrical and unsymmetrical isomers which are in dynamic equilibrium. The former contains two η^5-cyclopentadienyl rings, but the latter, which predominates in every case, exhibits one η^5- and one η^1-cyclopentadienyl group. The η^1 ring is 1,1-substituted by phosphorus and platinum, and there is a metal–metal bond which we formulate as a dative bond (Figure 1). An example of each isomeric form has been characterized by X-ray crystallography.[2] The fact that the molecules are fluxional at ambient temperature indicates that rearrangement between η^5- and η^1-cyclopentadienyl moieties is a facile process.

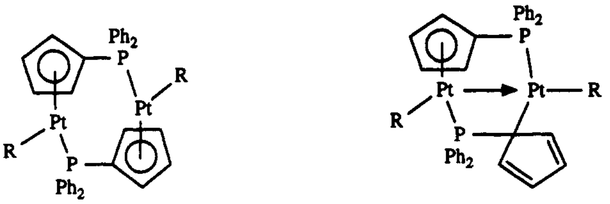

Figure 1. Structures of the symmetrical and unsymmetrical isomers of the complexes [$Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2$] (**1**).

In this paper we report the carbonylation chemistry of these dimers and their benzyl analogue **1e**. This work has allowed us to identify a number of other bonding modes for the dimetallic system bridged by dppc ligands. In addition, it provides a rare example of dinuclear reductive elimination from dimeric, organometallic complexes. A preliminary report of some aspects of this work has appeared.[8]

Results and Discussion

When carbon monoxide was bubbled through a CH_2Cl_2, $CHCl_3$, or C_6H_6 solution of [$Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2$] (**1a**) at ambient temperature, the yellow color was almost completely discharged within a few minutes. After workup the terminal carbonyl complex [$Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$] (**2a**) was isolated as a pale yellow solid in 90% yield (eq 1). The complex has been characterized by ^1H, ^{13}C, and ^{31}P NMR and infrared spectroscopy and by an X-ray diffraction study.

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1993.

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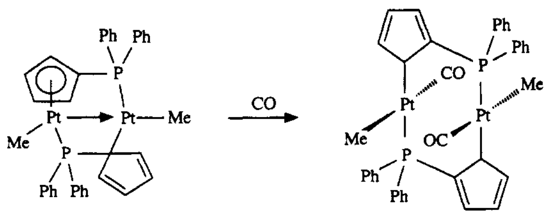

(1)

The $^{31}P\{^1H\}$ NMR spectrum of **2a** consists of a singlet with ^{195}Pt satellites, indicative of a symmetrical structure. The value of $^1J(Pt,P)$ is consistent with the phosphino group lying trans to a η^1-cyclopentadienyl group.[9] Its ^1H NMR spectrum exhibits a doublet for the methyl groups at 0.65 ppm, with a coupling to platinum of 63 Hz. There is also a doublet at 4.90 ppm ($^3J(P,H)$ = 7 Hz, $^2J(Pt,H)$ = 148 Hz) due to the hydrogen bound to the sp^3 carbon of the cyclopentadienyl ring and three other signals at 6.28, 6.60, and 7.40 ppm (the last is obscured by the aromatic resonances, but it has been assigned on the basis of a ^1H–^1H shift-correlated (COSY) 2D spectrum) due to the other hydrogens on the cyclopentadienyl ring. The $^{13}C\{^1H\}$ NMR spectrum contains a doublet at δ_C 2.7 ($^2J(P,C)$ = 7 Hz, $^1J(Pt,C)$ = 567 Hz) due to the methyl carbon. Signals for each of the protonated carbons of the cyclopentadienyl ring are observed and have been identified unambiguously by a ^{13}C–^1H shift-correlated (HETCOR) spectrum. The sp^3 carbon appears as a doublet of doublets at δ_C 60.5, whereas the other signals are in the aromatic region. Two sets of phenyl resonances are observed, indicating that the two phenyl groups on each phosphorus are nonequivalent. When the complex is prepared using ^{13}CO, a carbonyl resonance is found at δ_C 180.3 ($^2J(P,C)$ = 6 Hz, $^1J(Pt,C)$ = 1003 Hz). This is a fairly high δ_C value for a terminal carbonyl bound to platinum(II), but it is consistent with the CO lying trans to a high trans-influence ligand such as an organic group.[10] It exhibits a strong absorption at 2065 cm^{-1}, typical of a terminal carbonyl ligand.

Crystals of **2a** suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2/Et_2O solution. The molecular structure of **2a** is shown in Figure 2, and selected bond distances and angles are presented in Table 1. The coordination about each platinum atom is distorted square planar, and the dimer adopts a face-to-face structure with the two carbonyl ligands on opposite sides of the dimeric unit (*anti* to each other). The Pt–Pt distance is 3.157(1) Å, too long for any significant metal–metal interaction.[11] The distortion from square-planar geometry at platinum may be illustrated by the P–Pt–C(1) and C(14A)–Pt–C(19) angles of 97.3(5) and 85.9(5)°, respectively. The cyclopentadienyl group is coordinated through the sp^3 carbon, and the diene nature of the ring is illustrated by the shorter C(15)–C(16) and C(17)–C(18) distances. The Pt–C(14A) distance of 2.167(12) Å is longer than the platinum–methyl distance (2.091(12) Å). This difference in the bonding of the two sp^3-hybridized carbons has been discussed in terms of hyperconjugation of the cyclopentadienyl–metal bond with the diene residue of the ring.[12] The η^1-cyclopentadienyl group exhibits a weaker NMR trans influence than the methyl group, as evidenced by the larger $^1J(Pt,P)$ value for the P atom lying trans to the cyclopentadienyl group (2659 Hz) compared with those typically found for P atoms trans to CH_3 groups (1600–1800 Hz).[9]

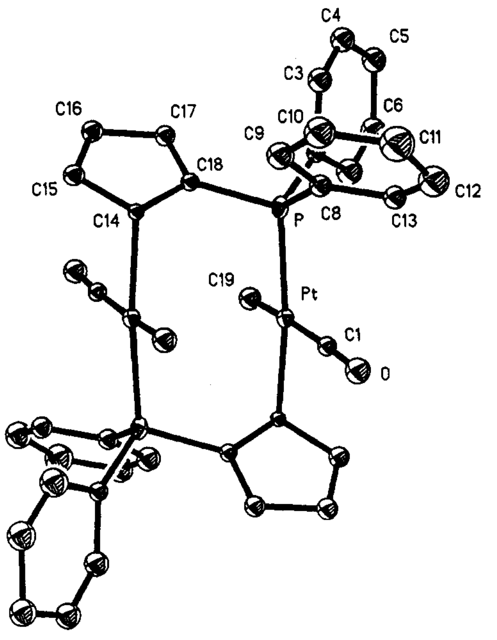

Figure 2. Projection view of the molecular structure of $[Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2a**) showing the atom-labeling scheme.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2a

	Bond Distances		
Pt–P	2.297(3)	Pt–C(1)	1.877(13)
Pt–C(14A)	2.167(12)	Pt–C(19)	2.091(12)
C(1)–O	1.155(17)	P–C(2)	1.835(11)
P–C(8)	1.834(11)	P–C(18)	1.799(13)
C(14)–C(15)	1.454(18)	C(14)–C(18)	1.509(17)
C(15)–C(16)	1.345(16)	C(16)–C(17)	1.405(20)
C(17)–C(18)	1.373(17)		
	Bond Angles		
P–Pt–C(1)	97.3(5)	P–Pt–C(14A)	171.6(3)
P–Pt–C(19)	86.4(4)	C(1)–Pt–C(14A)	88.9(5)
C(1)–Pt–C(19)	173.6(6)	C(14A)–Pt–C(19)	85.9(5)
Pt–P–C(2)	116.8(4)	Pt–P–C(8)	115.8(4)
Pt–P–C(18)	109.9(4)	PtA–C(14)–C(15)	110.4(8)
PtA–C(14)–C(18)	107.2(7)	C(15)–C(14)–C(18)	102.2(9)
C(14)–C(15)–C(16)	109.6(11)	C(15)–C(16)–C(17)	110.4(11)
C(16)–C(17)–C(18)	109.1(10)	C(14)–C(18)–C(17)	108.5(10)

Complex **2a** is soluble in CH_2Cl_2 or benzene but is sparingly soluble in ether or hexane. When this complex is isolated from CH_2Cl_2 solution by solvent removal, a small amount of CH_2Cl_2 is retained in the solid (0.6 molecule per dimer), which could not be removed by pumping under high vacuum. The presence of the appropriate amount of CH_2Cl_2 was confirmed by integration of the ^1H NMR spectrum. When the complex was isolated as single crystals from CH_2Cl_2/Et_2O solution, diethyl ether was retained in the crystal lattice.

Analogous reactions of $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1b–e**: R = Et, neo-Pe, Ph, Bz (CH_2Ph)) with carbon monoxide also generated face-to-face dimers of the form $[Pt_2R_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2b–e**). The phenyl and benzyl derivatives **2d** and **2e** are sparingly soluble in all solvents we have employed, and **2d** is insufficiently soluble for NMR characterization. The ethyl and neopentyl species **2b** and **2c** are slightly soluble in chlorinated solvents, but they are only sparingly soluble in benzene or toluene. Further reaction of **2b** and **2c** takes place at ambient temperature;

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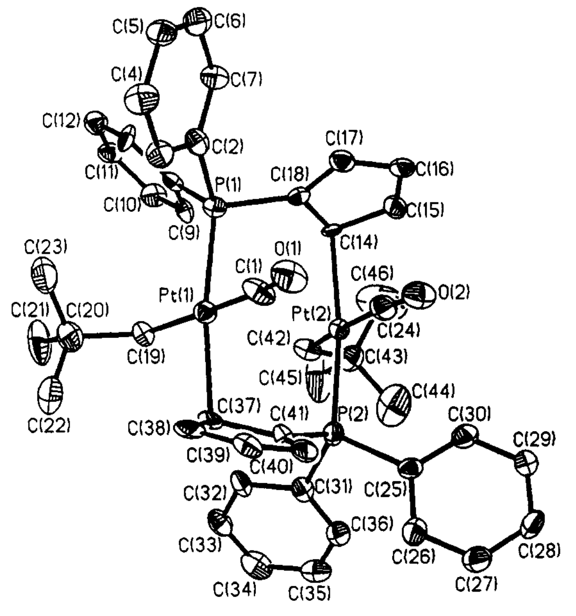

Figure 3. Projection view of the molecular structure of $[Pt_2(\text{neo-Pe})_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2c**) showing the atom-labeling scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2c

	Bond Distances		
Pt(1)–P(1)	2.308(3)	Pt(1)–C(1)	1.933(12)
Pt(1)–C(19)	2.108(11)	Pt(1)–C(37)	2.213(10)
Pt(2)–P(2)	2.298(3)	Pt(2)–C(14)	2.193(10)
Pt(2)–C(24)	1.903(13)	Pt(2)–C(42)	2.074(10)
P(1)–C(2)	1.829(11)	P(1)–C(8)	1.826(11)
P(1)–C(18)	1.813(11)	P(2)–C(25)	1.822(11)
P(2)–C(31)	1.826(11)	P(2)–C(41)	1.816(10)
C(1)–O(1)	1.133(14)	C(24)–O(2)	1.170(15)
C(14)–C(15)	1.462(16)	C(14)–C(18)	1.510(14)
C(15)–C(16)	1.363(16)	C(16)–C(17)	1.432(16)
C(17)–C(18)	1.354(16)	C(37)–C(38)	1.469(15)
C(37)–C(41)	1.500(15)	C(38)–C(39)	1.384(16)
C(39)–C(40)	1.419(15)	C(40)–C(41)	1.343(15)
	Bond Angles		
P(1)–Pt(1)–C(1)	89.6(4)	P(1)–Pt(1)–C(19)	92.4(3)
P(1)–Pt(1)–C(37)	170.5(3)	C(1)–Pt(1)–C(19)	174.0(4)
C(1)–Pt(1)–C(37)	89.6(5)	C(19)–Pt(1)–C(37)	89.4(4)
P(2)–Pt(2)–C(14)	171.2(3)	P(2)–Pt(2)–C(24)	89.2(4)
P(2)–Pt(2)–C(42)	93.3(3)	C(14)–Pt(2)–C(24)	89.4(5)
C(14)–Pt(2)–C(42)	89.4(4)	C(24)–Pt(2)–C(42)	171.0(5)
Pt(1)–P(1)–C(2)	114.9(4)	Pt(1)–P(1)–C(8)	121.4(4)
Pt(1)–P(1)–C(18)	106.1(3)	Pt(2)–P(2)–C(25)	113.2(4)
Pt(2)–P(2)–C(31)	119.0(4)	Pt(2)–P(2)–C(41)	106.9(4)
Pt(2)–C(14)–C(15)	104.5(7)	Pt(2)–C(14)–C(18)	106.6(6)
C(15)–C(14)–C(18)	103.2(9)	C(14)–C(15)–C(16)	109.6(10)
C(15)–C(16)–C(17)	109.2(10)	C(16)–C(17)–C(18)	109.4(10)
C(14)–C(18)–C(17)	108.4(10)	Pt(1)–C(37)–C(38)	105.9(7)
Pt(1)–C(37)–C(41)	107.1(7)	C(38)–C(37)–C(41)	103.2(9)
C(37)–C(38)–C(39)	109.3(10)	C(38)–C(39)–C(40)	107.9(9)
C(39)–C(40)–C(41)	111.0(10)	C(37)–C(41)–C(40)	108.4(9)

therefore, they must be isolated after short reaction times, or the solutions must be maintained at low temperatures. Both complexes have been characterized by ^{1}H, ^{13}C, and ^{31}P NMR and infrared spectroscopy (see Experimental Section), and **2c** has been the subject of an X-ray crystallographic investigation.

Crystals of $[Pt_2(\text{neo-Pe})_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2c**) were obtained from CH_2Cl_2 solution at −40 °C. Its structure is shown in Figure 3, and selected bond distances and angles are presented in Table 2. It also exists as a face-to-face dimer, but in contrast to **2a**, the molecule does not possess a center of symmetry since the two neopentyl groups are located on the same side of the dimeric unit (*syn* to one another). Each platinum atom exhibits distorted-square-planar geometry, and the two planes are inclined at approximately 5° to each other, bringing the carbonyl ligands into closer proximity and allowing the bulky neopentyl groups to achieve a greater separation from each other. The Pt–Pt distance of 3.315(1) Å is significantly longer than that in **2a** (3.157(1) Å), again reducing the steric interaction between the bulky alkyl groups.

Intuitively it might be expected that the *anti* form would be favored for the larger neopentyl groups, since this would permit them to be located as far apart as possible on opposite faces of the molecule, but it is the *syn* conformer that is obtained in the solid state. In contrast to **2a**, however, both conformers exist in appreciable amounts in solution for **2b** and **2c** (Table 3). In each case, two ^{31}P and two ^{31}C(CO) resonances are observed, separated in each case by about 1 ppm. The couplings to ^{195}Pt are identical for the two conformers. In fact, in benzene solution both conformers are observed for **2a** also, the ratio being approximately 20:1. This ratio changes to 4:1 for **2b** and 5:2 for **2c**. (The benzyl derivative complex **2e** exhibits two ^{31}P NMR signals in an approximate ratio of 1:1 (Table 3), but it is of quite low solubility). Thus, the ratio of the conformers becomes closer to unity as the size of the organic substituent increases. It appears that the difference in energy between the *syn* and *anti* forms becomes smaller as the size of the organic group increases, a finding which is quite unexpected. We cannot be certain, however, that it is the major component of the solution that crystallizes in each case. It is possible that the *syn* conformer is favored thermodynamically for **1a** but it is the minor, *anti* form which crystallizes, whereas the *anti* form becomes a larger component of the equilibrium mixture as the size of the organic substituent increases.

Solutions of **2a** are stable at ambient temperature. When a $CDCl_3$ or C_6D_6 solution of **2a** was heated to 50–55 °C *in vacuo*, however, a reaction occurred to produce the platinum(I) dimer $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**5**) and $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1a**) in a 2:1 ratio, along with propanone (δ_H 2.14 s (CH_3)). When the reaction was carried out under 1 atm of carbon monoxide, **5** and

Table 3. ^{13}C and ^{31}P NMR Data for the Complexes $[Pt_2R_2(^{13}CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (2)

	isomer 1				isomer 2				
R	δ_P	^1J(Pt,P), Hz	δ_C	^1J(Pt,C), Hz	δ_P	^1J(Pt,P), Hz	δ_C	^1J(Pt,C), Hz	ratio
Me[a]	12.5	2659	180.3	1103	b		b		
Me[c]	13.1	2630	182.0	1103	10.8	b	183.4	b	20:1
Et[d]	12.5	2822	181.1	1043	11.6	2822	181.9	1043	4:1
neo-Pe[e]	12.3	2766	179.3	997	11.1	2766	180.3	997	5:2
Bz[e]	12.6	2659			11.1	2659			1:1

[a] Recorded in $CDCl_3$ solution. [b] Not observed. [c] Recorded in C_6D_6 solution. [d] Recorded at in CD_2Cl_2 solution at −40 °C. [e] Recorded in d_8-toluene at −40 °C.

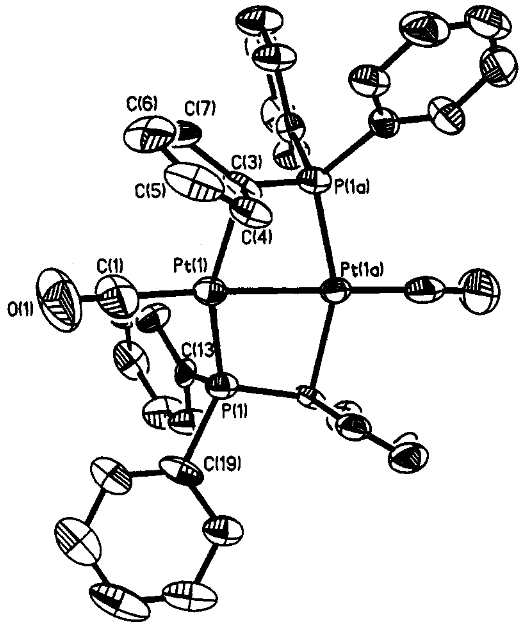

Figure 4. Projection view of the molecular structure of $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (5) showing the atom-labeling scheme.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 5

	Bond Distances		
Pt(1)–Pt(1A)	2.594(1)	Pt(1)–P(1)	2.254(3)
Pt(1)–C(1)	1.838(13)	Pt(1)–C(3)	2.225(9)
P(1)–C(3A)	1.735(11)	P(1)–C(13)	1.811(9)
P(1)–C(19)	1.872(11)	C(1)–O(1)	1.168(16)
C(3)–C(4)	1.460(15)	C(3)–C(7)	1.542(14)
C(4)–C(5)	1.363(16)	C(5)–C(6)	1.399(18)
C(6)–C(7)	1.396(17)		
	Bond Angles		
Pt(1A)–Pt(1)–P(1)	73.4(1)	Pt(1A)–Pt(1)–C(1)	175.7(5)
Pt(1A)–Pt(1)–C(3)	82.2(3)	P(1)–Pt(1)–C(1)	105.7(3)
P(1)–Pt(1)–C(3)	155.3(3)	C(1)–Pt(1)–C(3)	98.9(4)
Pt(1)–P(1)–C(3A)	105.0(3)	Pt(1)–P(1)–C(13)	112.9(3)
Pt(1)–P(1)–C(19)	120.9(4)	Pt(1)–C(3)–P(1A)	93.8(4)
Pt(1)–C(3)–C(4)	91.9(6)	Pt(1)–C(3)–C(7)	110.3(6)
C(4)–C(3)–C(7)	105.0(8)	C(3)–C(4)–C(5)	108.9(10)
C(4)–C(5)–C(6)	110.4(11)	C(5)–C(6)–C(7)	111.4(10)
C(3)–C(7)–C(6)	104.4(10)		

propanone were the only products obtained. Compound **5** is a yellow solid which is soluble in most common organic solvents. It has been characterized by ^1H, ^{13}C, and ^{31}P NMR and infrared spectroscopy and by X-ray diffraction.

The molecular structure of **5** is shown in Figure 4, and selected bond distances and angles are given in Table 4. The structure exhibits a center of symmetry, the dppc ligands being coordinated to one platinum through the P atom and to the other through the P-substituted carbon of the five-membered ring. This results in two four-membered Pt_2PC rings. The Pt–Pt distance is 2.594(1) Å, indicative of a strong metal–metal bond. The Pt–P and Pt–C(3) distances are 2.254(3) and 2.225(9) Å, respectively. The slightly shorter P–C(3) bond results in the four-membered ring adopting a distorted-trapezoid shape. The coordination about C(3) is distorted tetrahedral, the angles at C(3) ranging from 91.9(6) to 126.2(8)°. The PtA-Pt-P and PtA-Pt-C(3) angles are 73.4(1) and 82.2(3)°, respectively. The corresponding angles within the four-membered ring in **1a** are 68.1(1) and 82.9(2)°.[2] The smaller angle of 68.1° in **1a** suggests that the η^5-cyclopentadienyl group is more sterically demanding than the combination of η^1-cyclopentadienyl and carbonyl groups in **5**. The acute Pt–Pt–P angles in **1a** and **5** result in short, "nonbonded" contacts between Pt and P, 2.79 Å in **1a** and 2.90 Å in **5**. The CO ligands occupy terminal positions, resulting in an almost linear OC–Pt–Pt–CO unit.

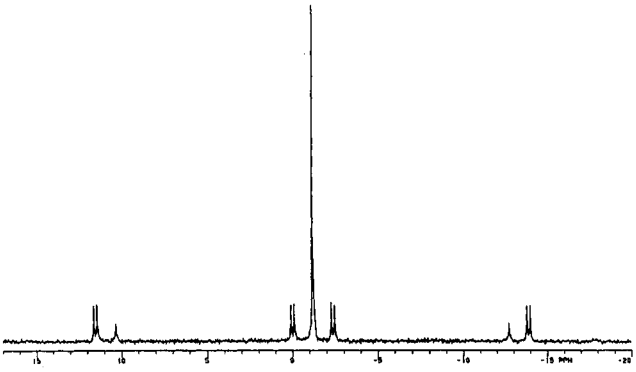

Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**5**) in $CDCl_3$ solution.

The $^{31}P\{^1H\}$ NMR spectrum of **5** (Figure 5) consists of a central singlet resonance, due to the isotopomer containing no ^{195}Pt, flanked by two sets of doublet satellites due to short-range (3085 Hz) and long-range (287 Hz) coupling to ^{195}Pt. The signals just inside the outer doublets arise from the $^{195}Pt_2$ isotopomer. The fact that these lines lie inside the doublets indicates that $^1J(Pt,P)$ and $^2J(Pt,P)$ have opposite signs.[13] Since $^1J(Pt,P)$ is generally assumed to be positive,[14] it follows that the two-bond coupling here is of negative sign. It has been pointed out that large, negative $^2J(Pt,P)$ values are found when there is a significant Pt–Pt interaction, whereas zero or small positive values are indicative of little metal–metal bonding.[15] The $^2J(Pt,P)$ value of −287 Hz is then consistent with the strong Pt–Pt interaction.

The ^1H NMR spectrum exhibits two multiplets for the C_5H_4 fragments, consistent with the presence of two pairs of equivalent hydrogens on each ring. The $^{13}C\{^1H\}$ NMR spectrum is also consistent with this structure and, in the ^{13}CO-labeled complex, the carbonyl carbon is again deshielded considerably and appears at 180.2 ppm. It exhibits short-range (1559 Hz) and long-range (125 Hz) couplings to platinum; in this case, the $^1J(Pt,C)$ and $^2J(Pt,C)$ couplings have the same sign. No coupling is observed between the carbonyl carbon and the adjacent P atom. This is not surprising, however, because $^2J(P,C)$ couplings between *cis* ligands are usually small.[10]

We have performed a number of experiments in order to elucidate the mechanism of the carbonylation/ketone-elimination reaction sequence. When a $CDCl_3$ solution of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1a**) was treated with CO at −40 °C, no reaction took place. When the solution was alternately warmed to 50 °C, then cooled to −40 °C, and examined by ^{31}P NMR spectroscopy, the only phosphorus-containing species observed during the course of the reaction were **2a** and the final product **5**. Thus, no intermediate species could be observed during the dinuclear reductive elimination of propanone from **2a**.

When the elimination reactions of the ethyl, neopentyl, and benzyl dimers were monitored by NMR spectroscopy, however, other species could be detected. When a $CDCl_3$

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(13) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1977**, *951.*

(14) McFarlane, W. *J. Chem. Soc. A* **1967**, 1922.

(15) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Seddon, K. R. *J. Organomet. Chem.* **1978**, *161*, C46.

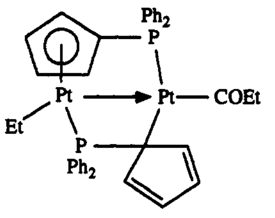

Figure 6. Structure of the complex [$Pt_2Et(COEt)(\mu$-$C_5H_4PPh_2)_2$] (**3b**).

Table 5. ^{13}C and ^{31}P NMR Data for the Complexes [$Pt_2R(COR)(\mu$-$C_5H_4PPh_2)_2$] (3)^a

R	δ_P	^1J(Pt,P), Hz	^2J(Pt,P), Hz	^2J(P,P), Hz	δ_C	^1J(Pt,C), Hz	^2J(Pt,C), Hz
Et	10.8 d	3871	173	18	212.3	1124	83
	−14.3 d	4436	446	18			
neo-Pe	10.4 d	3976	148	15	212.9	1109	98
	−16.4 d	4473	411	15			
Bz	11.0 d	3844	158	20			
	−17.4 d	4322	481	20			

^{a} Recorded in d_8-toluene solution.

solution of [$Pt_2Et_2(\mu$-$C_5H_4PPh_2)_2$] (**1b**) was treated with carbon monoxide, followed by evacuation of the NMR tube and heating to 55 °C overnight, analysis of the resulting solution by low-temperature ^{31}P and ^1H NMR spectroscopy showed that complex **5**, 3-pentanone (δ_H 1.03 t CH_3, 2.41 q CH_2, ^3J(H,H) = 7 Hz), and **1b** were present. When this reaction was repeated, but under a CO atmosphere, complex **5** was again produced, but a second dimeric species with ^{31}P NMR parameters similar to those of **1b**[2] was also observed. The $^{31}P\{^1H\}$ NMR spectrum of this complex, **3b**, consisted of two doublets, each of which exhibited short-range and long-range couplings to ^{195}Pt. When the reaction was performed using ^{13}CO, the high-frequency resonance displayed an additional coupling of 4 Hz, indicating the incorporation of one carbonyl ligand adjacent to the more deshielded P atom. Complex **3b** is assigned the structure shown in Figure 6. Consistent with this assignment was the observation of a ^{13}C resonance at 212.2 ppm, typical of an acylplatinum moiety.[10] This ^{13}C resonance also displayed one-bond and two-bond couplings to platinum. Analogous complexes were detected in the reactions of **1c** and **1e** with CO. The ^{31}P and ^{13}C NMR parameters for complexes **3b,c,e** are given in Table 5. The ^{31}P chemical shifts for each of these new complexes are very similar to those of the parent compounds **1b,c,e**, as is the ^1J(Pt,P) value for the P atom attached to the electron-rich platinum in each case. The one-bond coupling involving the P atom *cis* to the acyl group, however, is over 300 Hz smaller than that in the corresponding alkyl complex. The ^2J(Pt,P) values are greater in the acyl complexes, suggesting that the Pt→Pt dative bond is stronger in these complexes. As mentioned above, negative ^2J(Pt,P) values have been shown to be indicative of a significant Pt–Pt interaction.[15] In **1a**, where the signals arising from the $^{195}Pt_2$ isotopomer are not observed readily, we have determined from a ^{31}P–^{31}P COSY experiment[16] that the ^2J(Pt,P) couplings involving the Pt→Pt dative bond are negative. The two-bond couplings are presumably negative in the acyl complexes also.

Careful monitoring of the reactions of **1b** and **1c** with carbon monoxide allowed another intermediate to be observed and, in the case of the neopentyl derivative, to be isolated. When a CD_2Cl_2 solution of [$Pt_2Et_2(\mu$-$C_5H_4PPh_2)_2$] (**1b**) was treated with ^{13}CO at −78 °C and then warmed to −40 °C, no reaction occurred. Warming to ambient temperature for short periods of time (10–60 s), then cooling back to −40 °C, and monitoring by NMR spectroscopy first allowed the two conformers of **2b** to be observed. As the reaction proceeded, the acyl species **3b** was observed, along with a small amount of complex **5**. After a longer reaction time another unsymmetrical dimer, **4b**, appeared, which exhibited two ^{31}P doublet resonances and two ^{13}C carbonyl signals (Table 6). Further reaction resulted in **5** and 3-pentanone as the only observable products.

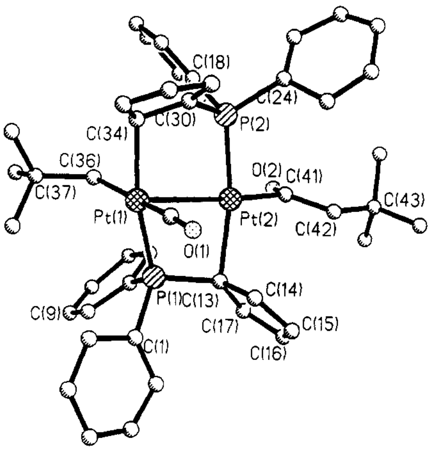

Figure 7. Projection view of the molecular structure of [Pt_2(neo-Pe)(CO)(CO-neo-Pe)(μ-η^1-$C_5H_4PPh_2)_2$] (**4c**) showing the atom-labeling scheme.

Table 6. ^{13}C and ^{31}P NMR Data for the Complexes [$Pt_2(COR)R(CO)(\mu$-$C_5H_4PPh_2)_2$] (4)^a

R	δ_P	^1J(Pt,P), Hz	^2J(Pt,P), Hz	^3J(P,P), Hz	δ_C	^1J(Pt,C), Hz	^2J(Pt,C), Hz
Et	11.2 d	3764	*b*	10	182.9	875	*b*
	21.7 d	2189	339	10	190.8	1002	106
neo-Pe	12.8 d	3866	84	21	183.5	882	*b*
	34.5 d	1922	549	21	194.0	988	91

^{a} Recorded in CD_2Cl_2 solution. ^{b} Not resolved.

The reaction of [Pt_2(neo-Pe)$_2(\mu$-$C_5H_4PPh_2)_2$] (**1c**) with ^{13}CO in $CDCl_3$ solution proceeded in a similar fashion. The two conformers of **2c** appeared first, followed by **3c** and some **5**, and then the new unsymmetrical dimer **4c**. In this case formation of **4c** was considerably faster than its reaction to form **5**; therefore, a significant concentration of **4c** developed. When such a solution was maintained at −40 °C for several days, crystals of **4c** precipitated from solution. When a solution containing a mixture of **3c** and **4c** was warmed to ambient temperature, complete conversion to complex **5** occurred, accompanied by reductive elimination of 2,2,6,6-tetramethylheptan-4-one (δ_H 2.65 s (CH_2), 1.01 s (CH_3)).

The molecular structure of **4c** is shown in Figure 7, and selected bond lengths and angles are presented in Table 7. The complex contains two η^1-cyclopentadienyl rings, but one is 1,1-substituted by P and Pt (as observed in the molecular structures of **1a**[2] and **5**), whereas the other is 1,2-substituted (as found in complexes **2a** and **2c**). The Pt–Pt distance of 2.780(3) Å, although slightly longer than that in **1a** (2.723(1) Å),[2] indicates the presence of a metal–metal bond. As in **1a**, this is formulated as a dative bond. The longer Pt–Pt distance is to be expected, however, because in this case the interaction is between a 16- and

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(16) Krevor, J. V. Z.; Simonis, U.; Karson, A.; Castro, C.; Aliakbar, M. *Inorg. Chem.* **1992**, *31*, 312.

Table 7. Selected Bond Distances (Å) and Angles (deg) for 4c

Bond Distances			
Pt(1)–Pt(2)	2.780(3)	Pt(1)–P(1)	2.299(8)
Pt(1)–C(34)	2.143(27)	Pt(1)–C(35)	1.886(34)
Pt(1)–C(36)	2.084(31)	Pt(2)–P(2)	2.241(9)
Pt(2)–C(13)	2.188(30)	Pt(2)–C(41)	2.073(37)

Bond Angles			
Pt(2)–Pt(1)–P(1)	68.7(3)	Pt(2)–Pt(1)–C(34)	98.3(9)
Pt(2)–Pt(1)–C(35)	90.9(11)	Pt(2)–Pt(1)–C(36)	97.9(10)
P(1)–Pt(1)–C(34)	166.9(9)	P(1)–Pt(1)–C(35)	97.2(9)
P(1)–Pt(1)–C(36)	91.0(9)	C(34)–Pt(1)–C(35)	84.8(12)
C(34)–Pt(1)–C(36)	88.5(11)	C(35)–Pt(1)–C(36)	169.7(14)
Pt(1)–Pt(2)–P(2)	83.7(3)	Pt(1)–Pt(2)–C(13)	82.4(9)
Pt(1)–Pt(2)–C(41)	168.1(9)	P(2)–Pt(2)–C(13)	165.6(10)
P(2)–Pt(2)–C(41)	94.4(9)	C(13)–Pt(2)–C(41)	100.0(12)

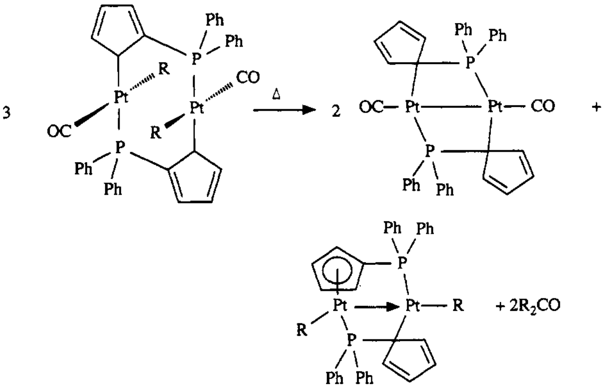
a 14-electron platinum center, whereas in **1a** the dative bond is between 18- and 14-electron moieties. In the [Pt$_2$Me$_3$(μ-dppm)$_2$]$^+$ cation,[17] which is also formulated with a Pt→Pt dative bond, the Pt–Pt distance is 2.769(1) Å. This also involves an interaction between 16- and 14-electron centers, but in this case the bridging dppm ligands occupy mutually cis positions at the electron-rich platinum center. In **4c** the geometry at Pt(1) is distorted square planar (analogous to that in **2c**), with the Pt→Pt bond occupying an axial site, whereas the Pt(2) coordination is similar to that in **1a** and **5**. The complex is also unusual in that it contains two carbonyl groups which function in different ways, namely, a terminal CO ligand on Pt(1) and an acyl group on Pt(2).

The NMR spectra of **4b** and **4c** (Table 6) may be explained on the basis of this structure. The δ_P and J(Pt,P) values for the P atom bonded to the electron-deficient platinum are not significantly different from those found for the corresponding P atom in **1b** or **1c**. The resonance due to the more deshielded P atom in **4b** is shifted by *ca.* 35 ppm to high frequency of that in **1b** and by *ca.* 9 ppm relative to **2b**. This may be explained in terms of a change in coordination of the cyclopentadienyl group from η^5 to η^1 in going from **1b** to **4b** and by distortion of the square-planar geometry about Pt(1) found in **2b** due to the presence of the Pt→Pt bond in **4b**. The latter may also account for the ^1J(Pt,P) value being significantly smaller than that in **2b**. These effects are paralleled, but in more striking fashion, in **4c**. The high-frequency ^{31}P resonance appears at δ_P 34.5, shifted by over 20 ppm compared with that in **2c**. The ^1J(Pt,P) coupling constant associated with this resonance is again reduced significantly from the value in **2c**, whereas the ^2J(Pt,P) value is greater than that observed in **1c**. The latter finding is unexpected in light of the proposed weaker Pt–Pt interaction and may indicate that the P–C–Pt coupling path makes a greater contribution to the coupling constant than that involving the metal–metal bond.

The ^{13}C resonances for the carbonyl groups in **4b** or **4c** may also be accounted for by this structure. The signals around 183 ppm in each complex are due to the terminal carbonyl ligands. These chemical shifts are very close to those found in **2b** or **2c**, again being at the high end of the range of Pt–CO species,[10] whereas the ^1J(Pt,C) values are reduced by *ca.* 100 Hz. The high-frequency resonances (190.8 ppm for **4b** and 194.0 ppm for **4c**) are representative of the acyl moieties. These chemical shifts are rather low for acylplatinum species,[10] but this may be due to the lack of a formal *trans* ligand (the Pt→Pt bond occupies the *trans* position). In general, the δ_C value for an acylplatinum moiety increases as the *trans* influence of the trans ligand increases.[10]

We have noted previously that there is a relatively facile interconversion of η^5- and η^1-cyclopentadienyl moieties in the complexes **1**.[2] It is also apparent from the work described here that such rearrangements are an important factor in the carbonylation reactions. It is also significant that the η^1 ring may be 1,1- or 1,2-substituted. Since η^1-cyclopentadienyls of platinum are usually fluxional,[18] it is not surprising that the metal here can migrate between the 1- and the 2-position. Further motion is, of course, prevented because the dppc ligand is anchored by coordination of the P atom. The ability of the cyclopentadienyl group of the dppc ligand to function as a 1,1- or 1,2-substituted η^1 moiety allows it the flexibility to support species with or without a Pt–Pt bond.

We have studied the thermolysis reactions of [Pt$_2$R$_2$(CO)$_2$(μ-η^1-C$_5$H$_4$PPh$_2$)$_2$] under various conditions in order to ascertain the rate-determining step in the reductive-elimination sequence. Two d_8-toluene solutions of each of the dimers **2a**, **2b**, **2c**, and **2e** were prepared (**2d** is insoluble and unsuitable for NMR study). One NMR tube was evacuated, and the other was evacuated and then filled with carbon monoxide (1 atm). The two samples were then treated identically throughout a heating/cooling/low-temperature ^{31}P NMR analysis cycle until the resonances for **2** had disappeared completely. In each case when the reaction was performed *in vacuo*, the dimer [Pt$_2$R$_2$(μ-C$_5$H$_4$PPh$_2$)$_2$] (**1**) was produced; this is necessary in order to achieve a mass balance of carbon monoxide (eq 2). Since the rates of reductive elimination from the four complexes are so different, the times of heating required were also different. The rates of reaction lie in the order **2c** (R = neo-Pe) > **2b** (Et) ≫ **2e** (Bz) > **2a** (Me), regardless of the presence or absence of CO. Both **2b** and **2c** react steadily at ambient temperature, whereas **2a** and **2e** require heating to temperatures above 40 °C to initiate reaction. In each case the signals due to the *syn* and *anti* conformers decreased in intensity at the same rate.



(2)

The following qualitative observations were made. For the methyl and ethyl complexes the reactions were inhibited by the presence of free CO.[19] With **2e** the initial reaction was slowed by the presence of free CO but after

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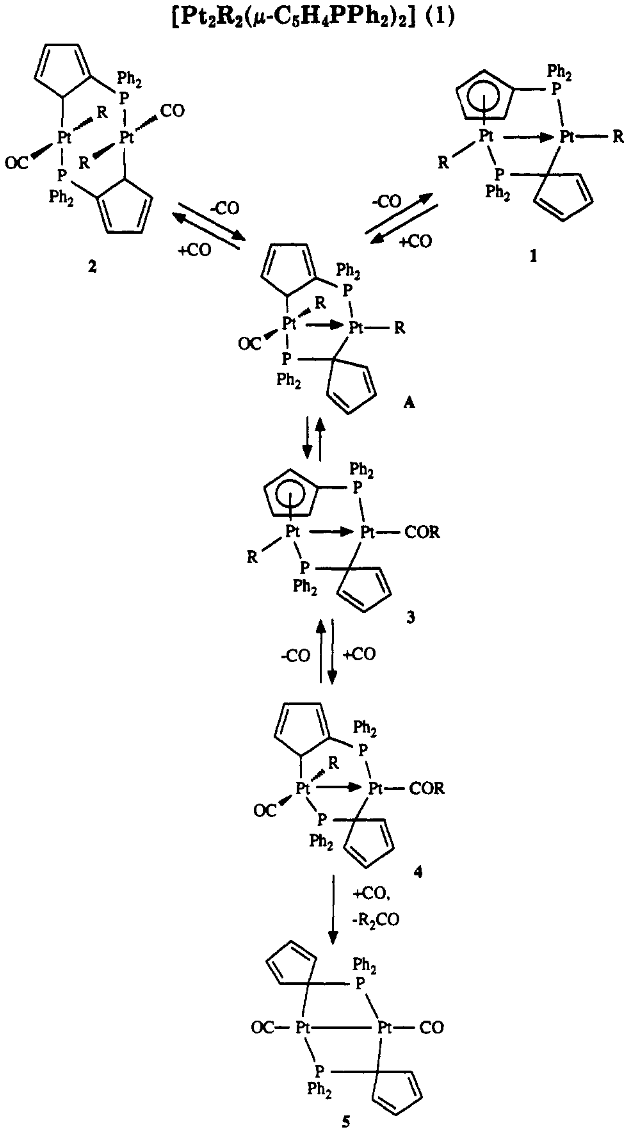
[17] Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500.

[18] Anderson, G. K.; Black, D. M.; Cross, R. J.; Robertson, F. J.; Rycroft, D. S.; Wat, R. K. M. *Organometallics* **1990**, *9*, 2568 and references therein.

Scheme 1. Mechanism of Carbonylation of $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (1)



a certain point appeared to proceed faster under CO. In this reaction the evacuated sample reacted faster until little **2e** remained. At this point the species present were **1e** and the phenylacetyl dimer $[BzPt(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)Pt(COBz)]$ (**3e**) (Table 5), in addition to 1,3-diphenylpropanone (δ_H 3.77 s (CH_2), 7.3–7.5 m (C_6H_5)). No intermediates were detected in the sample maintained under CO. In the case of $[Pt_2(\text{neo-Pe})_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2c**), both samples produced **4c** at approximately the same rate. When all of the starting complex **2c** had been consumed, the formation of complex **5** proceeded much more rapidly in the presence of free CO.

A proposed mechanism for the overall carbonylation/reductive-elimination sequence is shown in Scheme 1. The above observations suggest that the rate-determining step in the reductive-elimination reaction involves dissociation of CO from **2**, since the reactions of **2a**, **2b**, or **2e** are inhibited by the presence of free CO, probably to give a species of the form **A**. This intermediate, which has not been observed under any conditions but is related to the isolated acyl species **4**, would be formed by addition to CO to **1** or by loss of CO from **2**. Such a species would be a necessary intermediate in the stepwise addition to **1** of two CO groups to form **2**. The **1** → **A** step as depicted in Scheme 1 suggests that nucleophilic attack of CO occurs at the 18-electron Pt center, whereas one would anticipate that attack would occur at the more electron-deficient metal, but the ready rearrangement observed between η^5- and η^1-cyclopentadienyl species would render these indistinguishable. The **1** → **A** → **2** reaction sequence would be reversible and would permit the generation of **1** necessary in the reactions performed *in vacuo*. Species **A**, instead of simply gaining or losing CO, could undergo carbonyl insertion to produce the acyl dimer **3**. The addition of CO to **3** to generate **4** then parallels the first step in the carbonylation of the starting complex **1**. Each of the above steps may be reversible. The final step would be the irreversible reductive elimination of a ketone from **4** to generate **5**, promoted by addition of another CO molecule.

Since the reactions of **2a**, **2b**, and **2e** were slowed initially by the presence of free CO, loss of CO to form **A** would appear to be rate determining. In the case of **2c** the formation of **4c**, regardless of CO pressure, may indicate that the rates of the reactions to form **3** and **4** (which involve CO uptake) are great enough to balance the inhibition of the **2** → **A** process or that direct carbonyl insertion in **2c** to form **4c** can occur. The rate of the final step would be expected to be enhanced by the presence of free CO, and indeed this is found, most notably in the benzyl and neopentyl cases. Although **4c** is formed rapidly under CO and *in vacuo*, in the latter instance there is no external CO to facilitate the elimination, and conversion of some **4c** back to **1c** is necessary to provide the additional CO needed.

In the reactions performed *in vacuo* or under 1 atm of CO, diones were not formed, and no bis(acyl) complexes were identified during the course of the reactions. Attempts to prepare the bis(propionyl) complex $[Pt_2(COEt)_2(\mu\text{-}C_5H_4PPh_2)_2]$ by reaction of [PtCl(COEt)(COD)] with $TlC_5H_4PPh_2$ were unsuccessful.[20]

Since the reaction rates for the different R groups are significantly different, crossover experiments between **2a** and **2b**, for example, were uninformative. In this case reaction of **2b** occurred so much more rapidly that, at any given temperature, elimination from **2b** was complete before elimination from **1a** proceeded to any observable extent. Thus, heating a solution containing **2a** and **2b** to 55 °C resulted in elimination of propanone and 3-pentanone only. On the other hand, crossover experiments involving **2a** and **2a**-d_6, or **2b** and **2b**-d_{10}, did provide information about the intra- or intermolecular nature of the elimination process.

A 1:1 mixture of **1a** and **1a**-d_6 was dissolved in benzene and allowed to react with carbon monoxide to generate **2a** and **2a**-d_6. The reaction flask was then evacuated and maintained at 55 °C overnight. The gaseous products were analyzed by GC–MS (sufficient propanone is present in the gas phase to allow such analysis) and found to contain an approximately 1:2:1 mixture of d_0-, d_3-, and d_6-propanones. An analogous reaction involving **1b** and **1b**-d_{10} produced a 1:2:1 mixture of d_0-, d_5-, and d_{10}-pentanones. These results indicate that scrambling of the organic

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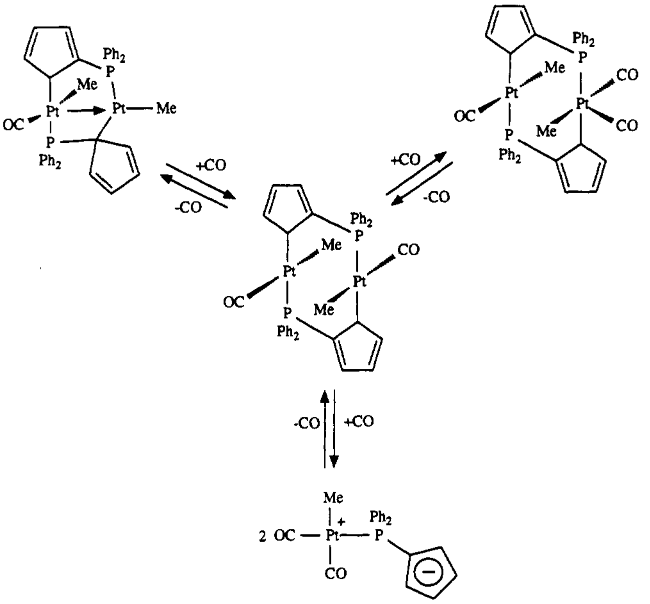
[19] The complexes $[Pt_2R_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (2) are of low solubility and are not completely in solution. This general lack of solubility, and the differences in solubility observed with different R groups, would not permit kinetic measurements of a quantitative nature to be performed.

[20] [PtCl(COEt)(COD)] may be prepared by treating the ethyl complex with 1 atm of carbon monoxide, but no reaction occurs when [PtClMe(cod)] is treated with CO at pressures up to 10 atm.

Table 8. Crystallographic Data for Complexes 2a, 2c, 4c, and 5

	2a	2c	4c	5
formula	$C_{38}H_{34}O_2P_2Pt_2 \cdot (C_2H_5)_2O$	$C_{46}H_{50}O_2P_2Pt_2 \cdot 2CH_2Cl_2$	$C_{46}H_{50}O_2P_2Pt_2 \cdot 2CH_2Cl_2$	$C_{36}H_{28}O_2P_2Pt_2$
mol wt	1048.9	1256.8	1256.8	944.7
color, habit	yellow, cubic	yellow, rectangular plates	orange, rectangular	yellow, rectangular
space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
a, Å	14.989(3)	11.879(5)	10.557(4)	21.229(3)
b, Å	16.031(4)	11.419(2)	13.237(6)	14.243(3)
c, Å	16.469(4)	35.125(6)	18.560(10)	21.065(3)
α, deg	90	90	106.66(4)	90
β, deg	104.31(2)	92.40(3)	98.62(4)	90.17(2)
γ, deg	90	90	98.15(3)	90
cell vol, Å^3	3834.5(15)	4760(2)	2409(2)	6369(2)
Z	4	4	2	8
D(calcd), Mg/m^3	1.817	1.757	1.730	1.970
temp, K	298	133	133	298
radiation	Mo K_α (λ = 0.710 69 Å)	Mo K_α (λ = 0.710 73 Å)	Mo K_α (λ = 0.710 73 Å)	Mo K_α (λ = 0.710 73 Å)
cryst dimens, mm	0.4 × 0.3 × 0.3	0.5 × 0.2 × 0.1	0.5 × 0.4 × 0.4	0.4 × 0.4 × 0.2
abs coeff, mm^{-1}	7.483	6.200	6.124	8.907
2θ range, deg	4.0–50.0	3.0–50.0	3.0–35.0	4.0–50.0
scan speed, deg/min	4.0–15.0	4.0–29.3	6.0–19.5	4.0–15.0
scan range (ω), deg	0.70 + K_α sepn	1.20 + K_α sepn	1.20 + K_α sepn	0.70 + K_α sepn
no. of indept rflns	3287	8420	3041	5576
no. of obsd rflns	1764 ($F > 6.0\sigma(R)$)	6043 ($F > 4.0\sigma(F)$)	2575 ($F > 4.0\sigma(F)$)	3295 ($F > 3.0\sigma(F)$)
abs cor	semiempirical	semiempirical	semiempirical	semiempirical
R	0.0288	0.0488	0.1120	0.0296
R_w	0.0348	0.0495	0.1454	0.0236
goodness of fit	0.75	1.40	0.96	0.91

Scheme 2. Possible Mechanisms for Exchange of Carbon Monoxide in $[Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (2a)



groups takes place at some point during the reaction sequence, probably by reversible dissociation into monomers. Alternatively, ketone formation could occur by coupling of an acyl group from one dimer with an alkyl group from another.

Crossover experiments using labeled and unlabeled CO are not feasible, because CO exchange in 2 occurs readily, but this may be associated with the dissociation mentioned above. Treatment of 1a with ^{13}CO produced $[Pt_2Me_2(^{13}CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$. Although elimination from this species does not occur at an appreciable rate below 50 °C, addition of unlabeled CO caused complete exchange of the carbonyl ligands within minutes at 25 °C. This exchange may occur in dissociative fashion *via* **A**, as discussed earlier, or by an associative process involving an 18-electron platinum center (Scheme 2). A third alternative is that the addition of CO causes cleavage of the dimeric unit to generate a zwitterionic species of the type $[PtMe(CO)_2(Ph_2PC_5H_4\text{-}P)]$. Such a species has not been detected with CO (the presence of two carbonyls and one phosphine in the square plane would be thermodynamically unstable), but we have observed, and in some cases isolated, complexes of the type $[PtRL_2(Ph_2PC_5H_4\text{-}P)]$ (L = py, CNBu^t, PR$_3$, P(OR)$_3$).[21]

Summary

We have demonstrated that the dppc ligand may adopt a number of different configurations in dimeric platinum complexes. In particular, we have prepared the first examples in which the cyclopentadienyl ring is coordinated in an η^1 fashion and shown that it may be 1,1- or 1,2-substituted by Pt and P. Carbonylation of the parent compounds $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (1) leads to terminal carbonyl and acyl complexes and, ultimately, to reductive elimination of a ketone and formation of the platinum(I) species $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**5**).

Experimental Section

NMR spectra were recorded on a Varian XL-300 FT NMR spectrometer. Chemical shifts are reported relative to TMS (^1H and ^{13}C) or H_3PO_4 (^{31}P). GC–MS data were obtained on a Hewlett-Packard 5988 instrument. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. The complexes $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (R = Me, Et, neo-Pe, Ph) were prepared as described previously.[2] The preparation of the benzyl analogue is described below. Carbon-13 monoxide (99% C-13) was purchased from Aldrich. CD_3I was purchased from Aldrich, and C_2D_5I was obtained from Cambridge Isotope Laboratories.

Preparation of $[Pt_2Bz_2(\mu\text{-}C_5H_4PPh_2)_2]$ (1e). To a solution of [PtClBz(COD)][22] (COD = cyclooctadiene) (0.461 g, 1.07 mmol) in benzene (50 mL) was added $TlC_5H_4PPh_2$ (0.539 g, 1.19 mmol) in small portions. The mixture was stirred under an argon atmosphere for 12 h and then filtered through an alumina column (50 × 30 mm, acidic, Brockman activity I, 80-200 mesh). The

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[21] Fallis, K. A.; Lin, M.; Anderson, G. K. *Organometallics*, in press.

[22] Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

Table 9. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2a

	x	y	z	U(eq)[a]
Pt	−316(1)	444(1)	738(1)	32(1)
P	738(2)	1431(2)	578(2)	34(1)
O(1)	−2011(7)	1335(7)	−279(6)	68(4)
C(1)	−1380(9)	987(9)	90(8)	53(5)
C(2)	1490(8)	1859(7)	1540(7)	40(4)
C(3)	2169(9)	2445(8)	1453(8)	52(5)
C(4)	2759(10)	2740(9)	2190(9)	64(6)
C(5)	2724(11)	2474(10)	2936(9)	70(6)
C(6)	2033(12)	1922(10)	3005(9)	74(7)
C(7)	1421(10)	1610(8)	2322(7)	53(5)
C(8)	259(8)	2386(7)	24(8)	39(4)
C(9)	494(8)	2672(8)	−678(8)	48(5)
C(10)	159(10)	3422(9)	−1054(9)	65(6)
C(11)	−449(11)	3859(9)	−705(12)	77(7)
C(12)	−696(11)	3579(10)	−37(11)	78(7)
C(13)	−353(10)	2835(9)	345(9)	62(6)
C(14)	1157(8)	617(7)	−870(6)	37(4)
C(15)	2027(9)	337(7)	−1054(8)	49(5)
C(16)	2743(8)	504(9)	−387(8)	49(4)
C(17)	2427(8)	885(8)	254(8)	48(5)
C(18)	1490(8)	1004(6)	−13(6)	31(4)
C(19)	764(8)	−194(8)	1540(7)	51(5)
O(2)	0	4609(23)	2500	281(33)
C(21)	1411(16)	4677(15)	2815(14)	151(13)
C(20)	691(20)	4171(19)	2524(20)	177(19)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

filtrate was concentrated, and pentane addition caused precipitation of a yellow solid, which was filtered and dried *in vacuo* (0.275 g, 48%). Anal. Calcd for $C_{48}H_{42}P_2Pt_2$: C, 53.83; H, 3.95. Found: C, 53.84; H, 3.97. ^1H NMR ($CDCl_3$, −40 °C; δ_H): 0.9, 1.0, 3.0, 3.4 br CH_2; 3.40, 4.19, 5.73, 6.11 (ring 1); 5.73, 6.55, 6.75, 7.08 (ring 2). $^{31}P\{^1H\}$ NMR (−50 °C): δ_{P_1} −15.6 d, $^1J(Pt_1,P_1)$ = 4152 Hz, $^2J(Pt_2,P_1)$ = 372 Hz, $^3J(P_1,P_2)$ = 20 Hz; δ_{P_2} 13.9 d, $^1J(Pt_2,P_2)$ = 4317 Hz, $^2J(Pt_1,P_2)$ = 128 Hz.

Preparation of $[Pt(CD_3)_2(COD)]$. To an ice-cold ether solution of $[PtI_2(COD)]$ (3.35 g, 6.01 mmol) was added an ether solution of CD_3Li (prepared from CD_3I and Li metal). The solution was stirred for 2 h and then hydrolyzed at 0 °C with a saturated aqueous solution of NH_4Cl. The ether layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined ether solution was dried over anhydrous $MgSO_4$ containing a small amount of charcoal. The solution was filtered and then evaporated, and the resulting white powder was dried *in vacuo* (1.12 g, 55%).

Preparation of $[PtCl(CD_3)(COD)]$. To a solution of $[Pt(CD_3)_2(COD)]$ (0.90 g, 2.65 mmol) in CH_2Cl_2/CH_3OH (2:1) was added acetyl chloride (0.188 mL, 2.65 mmol) dropwise. The mixture was stirred for 10 min, and the volume was reduced to 2 mL. Ether (10 mL) was added to give white crystals. After the temperature was lowered to 0 °C overnight, the solution was filtered, and the crystals were washed with pentane (3 × 5 mL) and dried *in vacuo* (0.79 g, 84%).

Preparation of $[Pt_2(CD_3)_2(\mu\text{-}C_5H_4PPh_2)_2]$ (1a-*d*₆). This complex was prepared in a manner analogous to that for the undeuterated species.[2]

Preparation of $[PtCl(C_2D_5)(COD)]$. To a stirred suspension of $[PtCl_2(COD)]$ (1.87 g, 5.00 mmol) in ether at 0 °C was added an ethereal solution of C_2D_5MgI, prepared from C_2D_5I (1.0 mL, 12.5 mmol) and Mg turnings (0.31 g, 12.8 mmol). The mixture was stirred for 2 h and then warmed to ambient temperature. After a further 1 h the mixture was quenched with 1 M NH_4Cl solution. The ether layer was separated and evaporated to dryness, leaving a yellow oil. The oil was dissolved in CH_2Cl_2 (25 mL), to which methanol (3 mL) was added. Acetyl chloride (0.37 mL, 5.0 mmol) was added dropwise, and the solution was stirred for 15 min. The solvent was removed, leaving the product as a yellow solid (0.924 g, 50%).

Table 10. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2c

	x	y	z	U(eq)[a]
Pt(1)	1347(1)	2017(1)	1340(1)	23(1)
Pt(2)	3939(1)	2450(1)	1060(1)	22(1)
Cl(1)	−1478(4)	4678(4)	104(1)	73(2)
Cl(2)	−2449(4)	2379(5)	230(1)	88(2)
Cl(3)	7300(3)	6428(4)	1090(1)	82(2)
Cl(4)	7641(5)	8219(4)	1668(2)	99(2)
P(1)	1666(2)	137(3)	1129(1)	23(1)
P(2)	3612(2)	4334(3)	1258(1)	23(1)
O(1)	479(7)	2673(7)	535(2)	41(3)
O(2)	2918(7)	3088(7)	271(2)	38(3)
C(1)	834(9)	2457(11)	831(3)	33(4)
C(2)	504(9)	−508(10)	842(3)	26(4)
C(3)	−578(9)	−46(10)	853(3)	29(4)
C(4)	−1465(10)	−589(11)	651(4)	39(4)
C(5)	−1287(10)	−1569(11)	439(3)	35(4)
C(6)	−217(10)	−2085(11)	432(3)	36(4)
C(7)	670(9)	−1530(10)	631(3)	28(4)
C(8)	2078(9)	−1037(9)	1459(3)	23(3)
C(9)	3092(9)	−957(10)	1683(3)	29(4)
C(10)	3391(9)	−1801(10)	1950(3)	30(4)
C(11)	2674(9)	−2739(9)	2006(3)	29(4)
C(12)	1676(9)	−2842(10)	1794(3)	29(4)
C(13)	1375(9)	−1964(10)	1527(3)	33(4)
C(14)	3983(9)	602(9)	893(3)	26(4)
C(15)	4506(9)	607(9)	524(3)	28(4)
C(16)	3711(9)	381(9)	242(3)	29(4)
C(17)	2652(9)	169(9)	409(3)	27(4)
C(18)	2780(9)	251(9)	793(3)	23(3)
C(19)	1728(9)	1552(10)	1912(3)	31(4)
C(20)	701(10)	1340(11)	2174(4)	37(4)
C(21)	1192(12)	844(15)	2554(4)	61(6)
C(22)	97(12)	2455(13)	2260(4)	58(5)
C(23)	−117(11)	441(12)	2010(4)	49(5)
C(24)	3236(9)	2821(10)	579(4)	34(4)
C(25)	4112(9)	5438(9)	931(3)	24(3)
C(26)	3787(9)	6620(10)	971(3)	32(4)
C(27)	4192(9)	7449(11)	721(3)	35(4)
C(28)	4916(10)	7123(10)	441(3)	35(4)
C(29)	5230(10)	5973(10)	403(3)	36(4)
C(30)	4820(9)	5128(10)	652(3)	31(4)
C(31)	4195(9)	4808(9)	1722(3)	25(3)
C(32)	3821(9)	4271(10)	2055(3)	28(4)
C(33)	4295(9)	4602(10)	2411(3)	31(4)
C(34)	5124(10)	5442(12)	2442(4)	40(5)
C(35)	5511(10)	5959(10)	2112(4)	36(4)
C(36)	5032(9)	5635(10)	1756(3)	28(4)
C(37)	1323(9)	3882(9)	1511(3)	25(4)
C(38)	202(9)	4323(9)	1390(4)	32(4)
C(39)	299(9)	5046(10)	1076(3)	28(4)
C(40)	1461(9)	5160(10)	1005(3)	28(4)
C(41)	2094(8)	4524(9)	1255(3)	23(3)
C(42)	4941(8)	2055(10)	1541(3)	27(3)
C(43)	6245(9)	2127(11)	1522(4)	34(4)
C(44)	6618(11)	3302(14)	1405(5)	70(7)
C(45)	6783(12)	1882(19)	1913(4)	90(8)
C(46)	6683(11)	1222(15)	1254(6)	89(8)
C(47)	−2159(13)	3730(13)	404(4)	62(6)
C(48)	8196(13)	7101(17)	1408(4)	78(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Preparation of $[Pt_2(C_2D_5)_2(\mu\text{-}C_5H_4PPh_2)_2]$ (1b-*d*₁₀). This was prepared according to the method used for the undeuterated species.[2]

Preparation of [PtCl(COEt)(COD)]. Carbon monoxide was bubbled through a benzene solution (20 mL) of [PtClEt(COD)] (0.330 g, 0.898 mmol) for 2 h. The solution was concentrated to 2 mL, and addition of pentane gave the product as a reddish brown solid (0.268 g, 75%). Anal. Calcd for $C_{11}H_{17}ClOPt$: C, 33.38; H, 4.33. Found: C, 33.47; H, 4.35. ^1H NMR ($CDCl_3$; δ_H): 1.01 t, CH_3; 2.70 q, CH_2; 2.2–2.7 br, CH_2 (COD); 4.53 m, *J*(Pt,H) = 80 Hz, *CH*; 5.77 m, *J*(Pt,H) = 25 Hz, *CH*. $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ_C): 8.9, CH_3; 27.2, *J*(Pt,C) = 30 Hz, CH_2 (COD); 31.5, *J*(Pt,C) = 30 Hz, CH_2 (COD); 46.4, CH_2; 85.8, *J*(Pt,C) = 238 Hz, CH

Table 11. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 4c

	x	y	z	U(eq)[a]
Pt(1)	–656(1)	4202(1)	1399(1)	17(1)
Pt(2)	383(1)	3437(1)	2560(1)	17(1)
P(1)	–762(8)	5306(7)	2588(5)	11(2)
P(2)	266(9)	1937(8)	1588(5)	20(3)
O(1)	2060(24)	5314(18)	1367(13)	32(6)
O(2)	–121(22)	2291(17)	3566(12)	27(6)
C(1)	–427(29)	6734(24)	2746(17)	8(8)
C(2)	–48(35)	7470(30)	3454(22)	36(11)
C(3)	–4(40)	8535(34)	3447(25)	52(12)
C(4)	–184(35)	8980(32)	2872(22)	39(11)
C(5)	–570(41)	8236(35)	2192(26)	58(13)
C(6)	–731(33)	7120(28)	2091(20)	27(10)
C(7)	–2277(28)	5078(23)	2938(16)	3(8)
C(8)	–3198(29)	5754(24)	2922(17)	12(9)
C(9)	–4393(27)	5554(22)	3144(15)	3(8)
C(10)	–4651(29)	4680(23)	3363(16)	8(8)
C(11)	–3815(28)	3918(23)	3319(16)	8(8)
C(12)	–2547(33)	4134(27)	3106(20)	27(10)
C(13)	432(30)	5079(25)	3277(18)	15(9)
C(14)	1880(30)	5603(24)	3326(18)	16(9)
C(15)	2479(31)	5984(24)	4095(18)	16(9)
C(16)	1624(28)	5809(22)	4534(17)	5(8)
C(17)	430(29)	5316(23)	4103(16)	6(8)
C(18)	–1236(29)	903(24)	1265(17)	11(9)
C(19)	–1821(31)	721(26)	1857(19)	21(9)
C(20)	–2972(38)	–18(30)	1693(23)	45(12)
C(21)	–3594(45)	–528(35)	926(25)	61(14)
C(22)	–2992(36)	–234(29)	368(22)	41(11)
C(23)	–1757(30)	454(24)	538(18)	18(9)
C(24)	1540(29)	1171(24)	1626(17)	9(8)
C(25)	1296(37)	94(29)	1469(20)	36(11)
C(26)	2304(36)	–435(30)	1583(20)	37(11)
C(27)	3531(33)	26(26)	1759(18)	22(9)
C(28)	3826(37)	1139(29)	1982(20)	34(11)
C(29)	2909(29)	1752(25)	1966(17)	12(9)
C(30)	454(30)	2367(24)	729(17)	11(9)
C(31)	1529(34)	2413(27)	434(20)	28(10)
C(32)	1321(33)	2988(25)	–70(18)	21(9)
C(33)	140(33)	3175(25)	–147(19)	22(9)
C(34)	–433(28)	2932(23)	436(16)	1(8)
C(35)	1028(33)	4861(26)	1362(18)	19(9)
C(36)	–2594(30)	3442(26)	1230(18)	21(9)
C(37)	–3607(29)	3696(23)	651(17)	11(8)
C(38)	–3488(35)	4928(26)	796(20)	36(11)
C(39)	–4948(39)	3300(32)	775(23)	54(12)
C(40)	–3591(41)	3217(32)	–191(22)	54(13)
C(41)	760(33)	2717(25)	3404(18)	15(9)
C(42)	2143(27)	3062(22)	3833(15)	0(8)
C(43)	2580(31)	2565(25)	4409(18)	19(9)
C(44)	2314(33)	1301(26)	4062(19)	27(10)
C(45)	3985(33)	3013(28)	4753(19)	29(10)
C(46)	1852(35)	2884(28)	5100(19)	31(10)
Cl(1)	8124(12)	225(10)	4358(7)	71(6)
Cl(2)	6222(11)	1208(9)	3639(6)	58(5)
Cl(3)	4308(12)	8800(9)	4099(7)	70(6)
Cl(4)	4132(15)	7754(10)	2476(8)	88(7)
C(47)	7700(32)	1468(26)	4315(19)	25(10)
C(48)	3411(42)	8506(35)	3203(23)	60(14)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 12. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 5

	x	y	z	U(eq)[a]
Pt(1)	111(1)	576(1)	1895(1)	33(1)
Pt(2)	601(1)	4503(1)	2599(1)	32(1)
P(1)	–932(1)	336(2)	2009(2)	35(1)
P(2)	467(1)	4738(2)	1555(1)	28(1)
O(1)	345(4)	761(10)	494(4)	123(6)
O(21)	2007(11)	4042(18)	2817(12)	54(7)
O(22)	2002(7)	4685(11)	2855(7)	74(5)
C(1)	244(5)	666(13)	1035(6)	80(6)
C(2)	1490(5)	4509(14)	2759(6)	106(7)
C(3)	1102(4)	713(7)	2228(5)	33(4)
C(4)	1119(4)	1707(8)	2060(5)	42(4)
C(5)	1506(5)	1823(9)	1551(6)	63(6)
C(6)	1766(5)	962(9)	1369(6)	65(6)
C(7)	1553(4)	233(8)	1756(5)	55(5)
C(8)	317(4)	4391(9)	3608(5)	33(4)
C(9)	520(5)	3409(8)	3601(5)	40(4)
C(10)	1052(5)	3354(9)	3968(5)	54(5)
C(11)	1201(5)	4222(9)	4209(5)	53(5)
C(12)	771(4)	4869(7)	4018(5)	34(4)
C(13)	–1155(4)	–883(6)	1912(5)	27(4)
C(14)	–730(4)	–1535(8)	1751(5)	42(4)
C(15)	–905(5)	–2448(8)	1641(5)	51(5)
C(16)	–1534(6)	–2726(8)	1714(6)	56(5)
C(17)	–1955(5)	–2061(8)	1897(6)	56(5)
C(18)	–1785(4)	–1164(7)	1975(6)	49(5)
C(19)	–1512(5)	885(8)	1450(6)	45(5)
C(20)	–1458(5)	776(9)	815(6)	60(5)
C(21)	–1910(6)	1108(8)	406(6)	65(6)
C(22)	–2425(6)	1570(10)	660(8)	77(7)
C(23)	–2479(5)	1691(9)	1288(7)	65(6)
C(24)	–2026(5)	1358(7)	1724(6)	45(5)
C(25)	986(5)	4149(7)	978(5)	33(4)
C(26)	758(5)	3542(7)	523(5)	40(4)
C(27)	1158(5)	3154(8)	85(5)	54(5)
C(28)	1791(5)	3377(9)	96(6)	55(5)
C(29)	2017(5)	3960(8)	552(6)	52(5)
C(30)	1634(4)	4375(8)	997(5)	48(4)
C(31)	562(4)	5954(7)	1332(5)	27(4)
C(32)	538(4)	6254(8)	709(5)	42(4)
C(33)	642(5)	7182(8)	540(6)	44(5)
C(34)	774(5)	7839(8)	1002(6)	47(5)
C(35)	812(4)	7544(8)	1628(6)	45(5)
C(36)	697(4)	6609(8)	1796(5)	43(4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(trans to Cl); 121.8, J(Pt,C) not observed, CH (trans to COEt). IR: ν(CO) 1674 cm^{-1}.

Reaction of [PtCl(COEt)(COD)] with $\mathbf{TlC_5H_4PPh_2}$. [PtCl(COEt)(COD)] (0.072 g, 0.18 mmol) was dissolved in benzene (20 mL) under argon. $TlC_5H_4PPh_2$ (0.15 g, 0.33 mmol) was introduced, and the mixture was stirred at ambient temperature for 24 h. $^{31}P\{^1H\}$ NMR analysis indicated that a large number of products had been formed.

Preparation of $\mathbf{[Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]}$ (2a). A CH_2Cl_2 solution of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (0.20 g, 0.22 mmol) was treated with CO (1 atm) for 5 min, and the solution turned green-yellow. The solvent was evaporated, and the product was dried *in vacuo* to leave $[Pt_2Me_2(CO)_2(\mu\text{-}C_5H_4PPh_2)_2]\cdot 0.6CH_2Cl_2$ as a yellow-green solid (0.19 g, 90%). Anal. Calcd for $C_{38.6}H_{35.2}Cl_{1.2}O_2P_2Pt_2$: C, 45.20; H, 3.46. Found: C, 45.01; H, 3.56. IR (KBr): ν(CO) 2065 cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C; δ_H): 0.65 d, ^3J(P,H) = 7 Hz, ^2J(Pt,H) = 63 Hz, CH_3; 4.90 d, ^3J(P,H) = 13 Hz, ^2J(Pt,H) = 148 Hz, 6.28, 6.60, 7.40, C_5H_4; 7.15–7.50, 7.72–7.85, C_6H_5. $^{13}C\{^1H\}$ NMR (δ_C): 2.7 d, ^2J(P,C) = 7 Hz, ^1J(Pt,C) = 567 Hz, CH_3; 60.5 dd, J(P,C) = 57, 22 Hz, 120.5 d, J(P,C) = 13 Hz, 134.4 dd, J(P,C) = 7, 4 Hz, 145.2 dd, J(P,C) = 12, 4 Hz, C_5H_4; 128.2 (2 overlapping doublets), J(P,C) = 10 Hz, *o*-CH; 129.8, *p*-CH; 130.6, *p*-CH; 131.6 d, J(P,C) = 12 Hz, *m*-CH; 138.8 d, J(P,C) = 12 Hz, *m*-CH; 180.3 d, ^2J(P,C) = 6 Hz, ^1J(Pt,C) = 1103 Hz, CO. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of an ether/dichloromethane (4:1) solution under an argon atmosphere.

Preparation of $\mathbf{[Pt_2Et_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]}$ (2b). Carbon monoxide was bubbled through a CHCl$_3$ solution of $[Pt_2Et_2(\mu\text{-}C_5H_4PPh_2)_2]$ (0.016 g, 0.034 mmol) at 0 °C for 20 min, during which time some solid precipitated. The solvent was evaporated to leave the product as a yellow solid (0.016 g, 94%). Anal. Calcd for $C_{38}H_{38}O_2P_2Pt_2$: C, 47.86; H, 3.82. Found: C, 47.80; H, 3.80. IR (KBr): ν(CO) 2062 cm^{-1}. ^{1}H NMR (CDCl$_3$; δ_H): 1.03 br s, CH_3; 1.27 br m, CH_2; 4.87 d, ^3J(P,H) = 13 Hz, ^2J(Pt,H) = 150 Hz, 6.41, 6.84 (remaining signal obscured by the phenyl resonances), C_5H_4; 7.25–7.55, 7.80–7.90, C_6H_5. (A doublet due to the minor isomer is detected at δ_H 5.00, ^3J(P,H) = 13 Hz; other signals are obscured).

Preparation of [Pt_2(neo-Pe)$_2$(CO)$_2$(μ-η^1-$C_5H_4PPh_2$)$_2$] (2c). This was prepared similarly from [Pt_2(neo-Pe)$_2$(μ-$C_5H_4PPh_2$)$_2$] (0.105 g, 0.203 mmol) and isolated as a yellow solid (0.108 g, 98%). Crystals suitable for an X-ray diffraction study were obtained from a CH_2Cl_2 solution at -40 °C.

Preparation of [$Pt_2Ph_2(CO)_2$(μ-η^1-$C_5H_4PPh_2$)$_2$] (2d). Bubbling carbon monoxide through a benzene solution of [Pt_2Ph_2(μ-$C_5H_4PPh_2$)$_2$] resulted in precipitation of a white solid within 5 min. IR: ν(CO) 2055 cm^{-1}.

Preparation of [$Pt_2Bz_2(CO)_2$(μ-η^1-$C_5H_4PPh_2$)$_2$] (2e). This was prepared from [Pt_2Bz_2(μ-$C_5H_4PPh_2$)$_2$] (0.085 g, 0.159 mmol) and isolated as a yellow solid (0.083 g, 92%).

Preparation of [Pt_2(neo-Pe)(CO)(CO-neo-Pe)(μ-η^1-$C_5H_4PPh_2$)$_2$] (4c). An NMR tube containing a $CDCl_3$ solution of [Pt_2(neo-Pe)$_2$(μ-$C_5H_4PPh_2$)$_2$] was evacuated and then filled with ^{13}CO (*ca.* 1 atm). The solution was maintained at -40 °C for several days, and crystals of **4c** precipitated from solution.

Preparation of [$Pt_2(CO)_2$(μ-η^1-$C_5H_4PPh_2$)$_2$] (5). A solution of [Pt_2Me_2(μ-$C_5H_4PPh_2$)$_2$] (0.90 g, 0.91 mmol) in benzene (50 mL) was treated with carbon monoxide (1 atm) for 5 min and then maintained at 55 °C for 12 h. The solution was then passed down on alumina column (80 × 10 mm). The resulting pale yellow solution was evaporated *in vacuo* to leave the product as a yellow solid (0.61 g, 70%). Anal. Calcd for $C_{36}H_{28}O_2P_2Pt_2$: C, 45.76; H, 2.97. Found: C, 45.87; H, 2.98. IR (KBr): ν(CO) 2050 cm^{-1}. ^1H NMR ($CDCl_3$; δ_H): 6.56 m, 6.72 m, C_5H_4; 7.15–7.45 m, C_6H_5. $^{13}C\{^1H\}$ NMR (δ_C): 122.6 m, ^2J(P,C) = 11 Hz, 128.5 m, C_5H_4; 128.3 m ^3J(P,C) = 11 Hz, *m*-CH; 130.7, *p*-CH; 132.5 m ^2J(P,C) = 13 Hz, *o*-CH; 135.3 m ^1J(P,C) = 50 Hz, *ipso*-C; 180.2 ^1J(Pt,C) = 1559 Hz, ^2J(Pt,C) = 125 Hz, ^2J(P,C) = 0 Hz, CO. $^{31}P\{^1H\}$ NMR (δ_P): -1.1, ^1J(Pt,P) = 3085 Hz, ^2J(Pt,P) = 287 Hz, ^3J(P,P) = 24 Hz.

Thermolyses of [$Pt_2R_2(CO)_2$(μ-η^1-$C_5H_4PPh_2$)$_2$]. In a typical reaction, 25–40 mg of the complex was placed in a NMR tube, to which d_8-toluene (0.4 mL) was added. The tube was then cooled to -78 °C, evacuated, and warmed to ambient temperature. The tube was either maintained under vacuum or filled with carbon monoxide (1 atm). Thermolyses of the ethyl and neopentyl derivatives were performed by alternately heating to 60 °C for 1 min, cooling to -40 °C, and monitoring by $^{31}P\{^1H\}$ NMR spectroscopy. The methyl and benzyl complexes required heating to 70–100 °C for 3–5 min to achieve a suitable reaction rate.

Crossover Experiments Involving Thermolysis of 2a and 2a-d_6. In a typical procedure, a mixture of **1a** (10.0 mg) and **1a**-d_6 (10.1 mg) was dissolved in C_6D_6 (0.8 mL) in a 5-mm NMR tube fitted with a stopcock. The solution was degassed, and CO was admitted to the tube. The stopcock was closed, and the tube was shaken for 1 min. This process was repeated; then the tube was degassed and heated at 55 °C overnight. A 0.1-mL aliquot was withdrawn from the gas phase by means of a gas syringe and analyzed by GC–MS.

Reactions involving **2b** and **2b**-d_{10} were carried out similarly.

X-ray Structure Determinations. Single crystals of appropriate dimensions of compounds **2a**, **2c**, **4c**, and **5** were mounted in random orientations for X-ray diffraction studies. The methods of data collection, structure solution, and refinement were carried out as described previously.[2,8] A summary of the crystallographic data is given in Table 8. Atomic coordinates and isotropic displacement coefficients for compounds **2a**, **2c**, **4c**, and **5** are given in Tables 9–12, respectively.

Data were collected at room temperatures for **2a** and **5**, whereas low-temperature (133 K) data sets were collected for **2c** and **4c**. The crystal lattice of **2a** contains one molecule of diethyl ether per platinum dimer, and **4c** has dichloromethane as the solvent of crystallization. The solvent molecules are not shown in the projection views. The asymmetric unit for **5** contains two half-molecules, one of which contains a disordered carbonyl group. Only one of the molecules of the asymmetric unit is presented.

Two data sets were collected for **4c**, one at ambient temperature and one at 133 K. Owing to the poor crystal quality and deterioration due to decomposition, data could only be collected up to $2\theta_{max}$ = 35° even at 133 K. Ineffective absorption correction and the poor-quality data resulted in a structure with strong residual peaks. No atom could be refined anisotropically except those in the solvent molecule. The results show the important features of the structure of this reaction intermediate, however, and are sufficient to establish its identity.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic displacement coefficients for non-hydrogen atoms, and calculated hydrogen atom coordinates and isotropic displacement coefficients for **2a**, **2c**, **4c**, and **5** (18 pages). Ordering information is given on any current masthead page.

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