ORGANOMETALLICS

Comparison of the Reactivity of Platinum(II) and Platinum(0) **Complexes with Iminophosphine and Phosphinocarbonyl Ligands**

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Supporting Information

ABSTRACT: Iminophosphines 2-(PPh₂)C₆H₄C(R)=NR' (L) (R = H, Me; R' = 2,6-Me₂C₆H₃ or 2,6-Prⁱ₂C₆H₃) react with Pt(II) precursors to form chelated *P*,*N* complexes [PtLX₂] (X = Me, Et, Cl), whereas with $[Pt(C_7H_{10})_3]$ (C_7H_{10} = norbornene) and other labile Pt(0) precursors coordination is via phosphorus and chelation is not observed. However, activation of the imine H or the methyl C-H bond of the ketoimine affords P,C metallacyclic hydride complexes

 $[PtH(PPh_2C_6H_4C=NR')L]$ and $[PtH(PPh_2C_6H_4C(=NR')CH_2)L]$, respectively. Under more forcing conditions the ketoimine complex undergoes a second metalation reaction, forming cis- and trans-bis-P,Cmetallacyclic complexes. By contrast, reaction of the phosphinocarbonyl ligands 2-(PPh₂)C₆H₄C(R)=O (L') (R = H, Me) with Pt(II) pre-



or six- (R = Me) membered P,C metallacyclic complexes, [PtMe(PPh₂C₆H₄CO)L']. On heating, the second phosphinocarbonyl metalates, forming cis- and trans-bis-P,C-metallacyclic complexes. X-ray crystallography of the cis-metalla-β-diketone complex

 $[Pt(PPh_2C_6H_4CO)_2]$ established the closeness of the carbonyl oxygen atoms, which readily capture H⁺ and other cations, forming stable complexes. These bis-chelate complexes also form readily from the reaction of the phosphinocarbonyls with $[Pt(C_7H_{10})_3]$ via an intermediate norbornyl complex (R = H) or a 5,6-ring bis-chelate (R = Me) in which a hydride is transferred from one ketone to partially reduce the second ketone.

INTRODUCTION

Heterodentate ligands with both hard and soft donor atoms have continued to attract interest due to their inherent properties.¹ Both iminophosphines and phosphinocarbonyl ligands have proven interesting due to the combination of a hard nitrogen or oxygen donor atom with a soft phosphorus donor. On coordination to transition metals, this hard/soft combination creates asymmetry in the metal orbitals, which then affects the reactivity of a complex containing one of these ligands. This can be illustrated by the difference in the trans influence of the phosphorus donor atom compared to nitrogen or oxygen. For example, in an iminophosphine complex the bond trans to the phosphorus is longer than that *trans* to the nitrogen, indicating the greater *trans* influence of phosphorus compared to the imine donor functionality.²⁻⁵ The hard/soft combination also leads to versatile coordination behavior with metal ions in different oxidation states and the potential for hemilability.⁶

While there are several examples in the literature of iminophosphines with different carbon backbones and substituents on the nitrogen,^{3,7–9} this research focused on bidentate iminophosphines of the type in Chart 1, as they have shown poten-tial as ligands in homogeneous catalysis.^{10,11} This type of Chart 1



iminophosphine allows the modulation of the steric crowding around the metal center through variation of the substituents on the imine nitrogen.¹² This is very useful for controlling the catalytic activity and selectivity of complexes containing these ligands.⁵ While a growing number of transition metal complexes of iminophosphines have been reported,^{6,12-18} there has not been a large amount of work published examining platinum complexes containing these iminophosphines. In particular

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Scheme 1



iminophosphines with a methyl group attached to the carbon of the imine group are notably rare.

2-(Diphenylphosphino)benzaldehyde is a structurally simple bidentate *P*,*O* chelating ligand. A variety of coordination modes have been reported for this ligand.⁸ First, it can act as a monodentate phosphorus ligand.¹⁹ It can also act as a bidentate chelating ligand, with the carbonyl portion bonded to the metal through either a σ -bond from the oxygen or the π -system of the carbonyl.^{19–21} This ligand has been observed to undergo chelateassisted oxidative addition of the C–H bond of the aldehyde group with several late transition metals in low oxidation states to give complexes containing a *P*,*C* chelate and a hydride ligand.^{21–24} While there have been a range of transition metal complexes of this ligand reported,^{8,19–25} there has not been the same investigation into the behavior of 2-(diphenylphosphino)acetophenone.^{26,27}

While C–H activation is a common reaction for the 2-(diphenylphosphino)benzaldehyde ligand, before 2002 it had not been observed for the iminophosphine ligands.^{28,29} Consequently we were interested in exploring this metalation reaction further in the iminophosphine ligand system, in particular, the effect of replacing the imine/aldehyde proton with a methyl group on the reactivity of both ligand systems toward C–H activation. Thus, here we report the synthesis and reactivity of previously unexplored platinum(II) and platinum(0) complexes containing these ligands.

RESULTS AND DISCUSSION

Reactions with Pt(II) Precursors. Reaction of iminophosphine ligands $(\mathbf{a}-\mathbf{c})$ with labile platinum(II) precursors such as $[PtX_2(dialkene)]$ (X = Me, Et, Cl; dialkene = cycloocta-1,5-diene (COD), hexa-1,5-diene) in equimolar ratios at room temperature resulted in the formation of simple *P*,*N* bidentate chelate complexes, $[PtX_2(PN)]$ ($1\mathbf{a}-3\mathbf{c}$) (Scheme 1). Analogous reactions have been reported previously.^{16,30} The new Pt(II) complexes reported here were characterized by elemental analysis, by detailed NMR spectroscopy, and, in the case of $2\mathbf{a}$, by single-crystal X-ray diffraction. The complexes are air stable in solution and in the solid state and were isolated as crystalline solids. All are typical coordination complexes of square-planar Pt(II) and display in their structural and spectroscopic properties the pronounced difference in *trans* influence of trivalent phosphorus and sp² imine nitrogen.

In each reaction, the formation of a platinum complex containing one of the iminophosphine ligands was confirmed by the ¹H, ¹⁵N, and ³¹P NMR spectra recorded of the reaction mixture. The ³¹P NMR spectra showed that the signal due to phosphorus had shifted 18–36 ppm downfield on coordination and had ¹⁹⁵Pt satellites (Table 1). The ¹⁹⁵Pt–³¹P coupling constant in each complex was found to vary depending on the ligand *trans* to the phosphorus donor.³¹ To confirm the coordination of nitrogen to the platinum, the ¹H NMR spectra were examined. In all cases the signal corresponding to the proton in the CH=N group showed ¹⁹⁵Pt satellites (Figure 1). By contrast, this coupling was not observed when the iminophosphine was acting as a monodentate ligand in the reactions with tris(norbornene)platinum (see below). Also, the CH=N signal in the ¹H NMR spectra was no longer a doublet, due to coupling to phosphorus, as it is in the free ligand.

Further confirmation that the nitrogen was coordinated to platinum was found in the ${}^{1}\text{H}-{}^{15}\text{N}$ heteronuclear multiple bond correlation (HMBC) spectra of the complexes. In each case the signal due to the nitrogen in the complex had shifted dramatically from that of the free ligand. For example, the signal appeared at -35.5 for **a**, while in complex **1a** it appeared at -115.8 ppm (Table 1). This significant low-frequency shift was consistent with that seen when similar nitrogen ligands, such as methyl and phenyl derivatives of 2,2'-bipyridine and 1,10-phenanthroline, coordinate to platinum(II). 32,33 The change in chemical shift and the observation of a correlation from the methyl ligands in complexes **1a** and **1b** to the imine nitrogen confirmed that the nitrogen was bound to the platinum.

Complex 2a was synthesized via reaction of [PtEt₂(COD)] with the dimethylphenyl P,N ligand a and was crystallized from Et₂O, affording orange crystals of sufficient quality for singlecrystal X-ray diffraction analysis. Details of the structural solution and refinement are given in Table 2, and key molecular parameters appear in Table 3. The molecular structure of 2a is shown in Figure 2 and confirms the proposed structure, showing the iminophosphine ligand acting as a chelating bidentate ligand. The bite angle of the iminophosphine ligand $(88.38(5)^{\circ})$ is comparable to that reported for similar complexes of iminophosphines with the same backbone including [PtMe₂L] (86.8(1) $^{\circ}$), $[PtCl_2L] (88.39(8)^{\circ}) (L = N - [\{2 - (diphenylphosphino)phenyl\}]$ methylene]-[6,6-dimethyl-{1S- $(1\alpha,2\beta,5\alpha)$ -bicyclo[3.1.1]heptane}]-2-methaneamine),³⁴ and [PdCl₂(2-(PPh₂)C₆H₄CH=N(C₆H₅))] $(86.34(8)^{\circ})$.¹⁶ The bond between the platinum and the carbon *trans* to phosphorus (2.102(2) Å) is longer than that *trans* to nitrogen (2.0546(18) Å). The Pt(1)–P(1) bond length of 2.2543(5) Å is comparable to that reported for $[PtMe_2L]$ (2.244(1) Å),³⁴ and the Pt(1)-N(1) bond length of 2.140(2) Å is in the range found for similar complexes where the imine is trans to a methyl group. 30,34,35

Reaction of Pt(II) precursors with an excess of the P,N ligand afforded products with only one P,N ligand coordinated to the metal. Thus for the P,N ligands studied here, chelation is strongly preferred over monodentate coordination when the metal is in the +2 oxidation state. In contrast to the iminophosphine ligands, the phosphinocarbonyl ligands **d** and **e** did not form chelated P,Ostructures under any conditions investigated in this study.

The initial product of the reaction of the phosphinoaldehyde **d** with [PtMe₂(hexa-1,5-diene)] is the nonchelated intermediate *cis*-[PtMe₂(PPh₂C₆H₄CHO)₂] (**4d**), readily characterized by ¹H and ³¹P NMR spectroscopy (Scheme 2). In solution this complex readily converts into the monometalated complex **5d** with the elimination of methane (observed at 0.22 ppm in the ¹H NMR spectra) and formation of a five-membered *P*,*C* metallacycle. The ³¹P NMR spectrum of **5d** shows two doublets at 51.4 and 18.8 ppm (²J_{PP} = 5.2 Hz) with ¹⁹⁵Pt satellites. The small value of ²J_{PP} indicates a *cis* relationship between the phosphorus atoms, and the high chemical shift of one signal is indicative of a five-membered ring.³⁶ Upon refluxing in toluene for 16 hours, a second metalation takes place, affording a mixture of the *cis* and *trans* isomers of **6d** with two five-membered metallacyclic rings.

Table 1. Selected NMR Data of the Platinum Complexes

			CR=N/O				
compound	$\delta^{31}\mathrm{P/ppm}$	$J_{\rm PtP}$ /Hz	δ^1 H/ppm (J/Hz)	$J_{\rm PtH}/{\rm Hz}$	δ^{13} C/ppm (J _{PC} /Hz)	$J_{\rm PtC}/{\rm Hz}$	δ^{15} N/ppm
a	-14.0		8.90 (d, 5.6)				-35.5
ь	-15.0		8.94 (d, 5.6)				-37.3
с	-9.3		1.77 (d, 1.5)		164.0		-31.0
d	-10.9		10.50 (d, 5.4)				
e	-2.7		2.02		198.2		
la	21.8	1921	7.73	39			-115.8
1b	21.8	1913	8.15	39			-116.3
1c	24.0	1892	1.35		166.8 (d. 5.9)		-112.6
2a	22.2	1765	7.65	31			
2b	22.2	1755	8.12	32			
2c	23.4	1725	1.33 (d. 0.9)	0-			-107.5
3a	2.4	3668	8.33	111			
3b	2.9	3654	8 39	109			
30	2.5	3679	2.02	10)	171.3(d.6.8)		-160.3
4d	23.7	1831	10.69(d.2.3)		1,110 (4,010)		10010
4e	33.1	2067	1.86				
5d	51.4 (d. 5.2)	2088	10.47 (d. 2.5)		232.5 (d. 133.0)	1080	
04	18.8(d, 5.2)	1558	10117 (0,210)		190.2 (d. 13.2)	1000	
50	33.4(d, 10.8)	2828	2,39		1)0.2 (u) 10.2)		
50	22.1(d, 11.0)	1888	2.57				
6c-cis-trans	10.5	2191	2.45(t.82)	99			
oe dis truits	13.7	2901	3.18(t, 6.5)	79			
6d-cis	47.8	1843	5.10 (1, 0.5)	//	а	а	
6d+H ⁺	45.2	2114			250 5 (d 108 8)	991	
6e-cis-trans	18.0	2459	260(+63)	82	201 4	52	
00-013-014013	17.5	2432	3.38(dd, 7.3, 2.2)	93	201.4	52	
73	21.9	3203	8.94 (d. 2.6)	75			а
7a 7b	22.0	3243	9.00(d, 2.3)				а
76 76	22.0	3272	9.00 (u, 2.3)				а
70	20.0	35/15	1.78				
7e 8a	20.4	3533	0.08				а
8b	29.4	35/3	9.00				а
80	25.7	3708	9.11 a	а	a	а	а
80	38.2	3851	1.05				
92	49.2 (m)	1010	9.60(3.28)				а
94	204(d, 7, 9)	1919	9.00 (u, 2.0)				
oh	20.4(u, 7.9)	1910	928(421)				а
90	72.0 (m)	1910	9.20 (u, 2.1)				
96	22.9 (111)	2559	1 75		174.9		а
90	15.9	1707	1./5		1/4.0		
90	13.6	2952	2.71(+.10.2)	05			
96	29.0(d, 10.7)	1808	5./1 (t, 10.2)	93			
10.5	17.1 (u, 10.7)	2612	1 66				а
110	27.3	3012	1.00				а
120	33.7 12 1	377/	0.11				
124	45.0	1604	7.11				
130	43.0	1642	10.37 (U, 2.7)				
14e	10.3	2072	116 (td 80 11)	00	100.8(+.60)		
140	(u, 0.1)	1525	4.10(10, 0.0, 4.1)	90 00	177.0(1,0.0)		
	17.2 (u, ð.1)	1323	3.00 (lu, 9.4, 4.1)	00	1/0.9 (u, 34.9)		

^{*a*} NMR data could not be obtained.



Figure 1. Low-field section of the ¹H NMR spectrum of 1a.

Table 2. Crystallographic Data

	2a	cis- 6d · C ₆ H ₆	9b	
chemical formula	C ₃₁ H ₃₄ NPPt	$C_{44}H_{34}O_2P_2Pt$	$\mathrm{C}_{62}\mathrm{H}_{64}\mathrm{N}_{2}\mathrm{P}_{2}\mathrm{Pt}$	
formula weight	646.65	851.74	1094.17	
<i>a,</i> Å	9.4923(4)	13.6485(11)	13.3764(5)	
<i>b,</i> Å	11.1549(4)	18.4002(13)	34.9788(12)	
<i>c,</i> Å	14.5403(8)	14.5882(11)	13.1827(5)	
α , deg	103.134(2)	90	90	
β , deg	104.928(2)	112.622(4)	102.833(2)	
γ, deg	107.442(2)	90	90	
<i>V</i> , Å ³	1339.61(10)	3381.7(4)	6014.0(4)	
Ζ	2	4	4	
space group	<i>P</i> -1	C2/c	$P2_1$	
<i>Т,</i> К	121	118	118	
$d_{\rm calcd}$, g cm ⁻³	1.603	1.673	1.208	
μ , cm ⁻¹	5.316	4.283	2.422	
$R_1 \left[I > 2\sigma(I) \right]^a$	0.021	0.045	0.049	
wR_2 (all data) ^a	0.057	0.145	0.094	
¹ Definition of R indices: $R_1 = \Sigma^{ } F_0 - F_c ^{ } / \Sigma F_0 $; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.				

The ³¹P NMR spectrum of *cis*-**6d** has one singlet at 47.8 ppm with ¹⁹⁵Pt satellites (Table 1). Similarly, **d** has been observed to undergo chelate-assisted oxidative addition with [{IrCl(cod)}₂] to produce octahedral irida- β -diketones.³⁷ Metalla- β -diketones where the carbonyl groups are not stabilized by chelation have also been prepared by Lukehart³⁸ and Steinborn.³⁹

In a similar manner **e** reacts readily with [PtMe₂(hexa-1,5diene)] in chloroform to form a bis-monodentate intermediate before reacting further to form a complex with one six-membered ring metalated at the ketone methyl group, **5e** (Scheme 3). The ³¹P chemical shifts are 33.4 and 22.1 ppm, the latter being typical of phosphorus involved in a six-membered metallacycle.³⁶ Further reaction in chloroform at reflux leads to doubly metalated *cis* and *trans* isomers of **6e**.

Reactions with Pt(0) Precursors. As catalysis with Pd and Pt often involves both the 0 and +2 oxidation states of the metals, we investigated the behavior of the iminophosphine and phosphino-carbonyl ligands with Pt(0) precursors. Separate reactions of tris-(norbornene)platinum(0) (norbornene = bicyclo[2.2.1]heptene) and the ligands **a**, **b**, and **c** in 1:1, 1:2, and 1:3 ratios were carried out. These reactions resulted in mixtures, and the products were

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 2a

Pt(1)-P(1) Pt(1)-N(1) Pt(1)-C(1) Pt(1)-C(3)	2.2543(5) 2.1400(16) 2.0546(18) 2.102(2)	N(1)-C(5) N(1)-C(13) P(1)-C(15)	1.444(3) 1.283(3) 1.8260(18)
P(1)-Pt(1)-N(1)	88.38(5)	P(1)-Pt(1)-C(3)	174.31(7)
C(1) - Pt(1) - C(3)	87.50(8)	C(5)-N(1)-C(13)	113.78(16)
P(1)-Pt(1)-C(1)	93.21(6)	Pt(1)-N(1)-C(5)	118.21(13)
$N(1){-}Pt(1){-}C(3)$	91.51(7)	Pt(1)-N(1)-C(13)	127.96(14)
N(1) - Pt(1) - C(1)	173.90(7)		

identified by ¹H and ³¹P NMR spectroscopy in solution. Kurosawa et al. reported a similar investigation with less sterically hindered ligands, and our observations are broadly in accord with their findings.²⁹

The initial formation of $[Pt(P)(nb)_2]$ (7a) and $[Pt(P)_2(nb)]$ (8a) (P = a acting as a monodentate phosphorus ligand, nb =norbornene) (Scheme 4) was observed in all of the reactions of a. The signals for the complexes in the ³¹P NMR spectra of the reactions appeared as singlets at 21.9 (${}^{1}J_{PtP}$ = 3203 Hz) and 29.4 ppm $({}^{1}J_{PtP} = 3533 \text{ Hz})$ for 7a and 8a, respectively (Table 1). This is consistent with the ³¹P NMR data of the analogous complexes with triphenylphosphine⁴⁰ and that of $[Pt(P)_2(nb)]$ (where P = $2-(PPh_2)C_6H_4CH=N((CH_2)_2C_6H_5))$.²⁹ The signals for the CH=N group in the ¹H NMR spectra did not have ¹⁹⁵Pt satellites, which were present in all of the platinum(II) complexes where the ligands were acting as bidentate ligands. Interestingly, no tris(phosphine) complex $[Pt(P)_3]$ was observed in these reactions, even when carried out in a 1:3 complex/ligand ratio. This is in contrast with Kurosawa's work, where a tris(phosphine) complex was observed initially in the 1:3 reaction.²⁹ We ascribe this to the greater bulk of the ligands used in this study.

After one day all reactions showed the formation of a third complex, which was identified as the hydride complex **9a**. This hydride complex was formed from the metalation of the CH=N group on one of the ligands in **8a**. The signal due to the hydride ligand appeared in the ¹H NMR spectra of the reaction mixture at -2.83 ppm as a doublet of doublets with ¹⁹⁵Pt satellites. The ²J_{PH} coupling constants of 176 and 29 Hz were consistent with the hydride coupling to two different phosphorus nuclei, one in a *cis* position and the other *trans*. The ³¹P signals of these phosphorus nuclei appeared at 49.2 and 20.4 ppm; the high chemical shift of the former signal is consistent with the formation of a five-membered metallacycle. This type of reactivity of the CH=N group has been reported twice in the literature in Pt complexes^{29,41} and once in a Co complex.²⁸

The reactivity pattern of ligand **b** with tris(norbornene) platinum is identical to that of ligand **a**. Thus, the extra bulk of the isopropyl groups did not interfere with the formation of the hydride complex **9b**. Crystals of a quality sufficient for use in X-ray analysis were grown by the inward diffusion of hexane into a Et_2O solution of **9b** in the presence of a small amount of cycloocta-1,5-diene at 4 °C. Single-crystal X-ray crystallography confirmed the proposed structure of **9b**, showing metalation of one of the iminophosphine ligands and monodentate coordination of the other (Figure 3). Details of the structural solution and refinement are given in Table 2, and selected bond lengths and angles are given in Table 4. The platinum in this structure is disordered, occupying

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Figure 2. ORTEP diagram of 2a showing 50% probability thermal ellipsoids. H-atoms have been omitted for clarity.



Scheme 3^a



^{*a*} Ar = $C_6H_4CH=O$.

two different positions. Figure 3a shows the site with 85% occupancy. When the platinum is occupying the other site, the ligands switch coordination modes (Figure 3b), with the monodentate ligand now chelated and *vice versa*. While the hydride ligand was not found, given that the arrangement of the other ligands around the platinum is square planar, its position can be inferred. The bite angle of the metalated ligand is 79.2°. This is comparable to that reported by Kurosawa (82.1°)²⁹ and that reported in the Co complex containing a similar iminophosphine ligand (79.1°).²⁸

In the reaction of ligand **c** with tris(norbornene)platinum the formation of the analogous hydride complex **9c** was more facile with a significant amount present in solution after one hour. This complex was identified by the hydride signal at -4.17 ppm (${}^{2}J_{PH}$ = 196, 28, ${}^{1}J_{PtH}$ = 1145 Hz) in the 1 H NMR spectrum and two signals in the 31 P NMR spectrum at 28.6 and 15.8 ppm. The lack of PP coupling for the two signals in the 31 P spectrum and the









Figure 3. (a) ORTEP diagram of 9b showing the platinum site with 85% occupancy. (b) ORTEP diagram of 9b showing the platinum site with 15% occupancy. 50% probability thermal ellipsoids are shown. H-atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 9b

Pt(1) - P(1)	2.305(2)	C(2) - C(3)	1.414(12)
Pt(1) - P(2)	2.307(2)	P(1)-C(3)	1.797(8)
Pt(1) - C(1)	2.087(7)	N(2) - C(50)	1.348(9)
N(1)-C(1)	1.344(8)	N(2) - C(51)	1.391(12)
N(1) - C(20)	1.424(9)	C(50)-C(49)	1.492(12)
C(1) - C(2)	1.469(12)		
P(1)-Pt(1)-C(1)	79.2(2)	C(2)-C(1)-N(1)	116.5(6)
P(1)-Pt(1)-P(2)	113.24(7)	C(1)-N(1)-C(20)	121.3(6)
P(2)-Pt(1)-C(1)	166.5(2)	C(49) - C(50) - N(2)	118.1(8)
Pt(1)-C(1)-N(1)	125.8(6)	C(50)-N(2)-C(51)	116.9(7)
Pt(1)-C(1)-C(2)	117.2(5)		111.3(5)

magnitude of the ${}^{1}J_{PtP}$ confirm the *cis* geometry. In contrast to the reactions of **a** and **b** this reaction proceeds to form the bis-chelate complex **6c** as a mixture of *cis* and *trans* isomers. However, this reaction never goes to completion, and the reaction results in a mixture of the two isomers of **6c** and **9c**.

When **c** is reacted with tris(ethene)platinum, the bis- and monoethene complexes $[Pt(P)(C_2H_4)_2]$ (**10c**) and $[Pt(P)_2(C_2H_4)]$ (**11c**) are formed first (Scheme 5). The ³¹P and ¹H NMR data of these complexes are in accord with those reported for analogous complexes with triphenylphosphine (Table 1).^{42–44} This reaction goes on to form **9c** and then finally the *cis* and *trans* isomers of **6c**. It is important to note that this reaction always contains a mixture of products, and heating the reaction resulted in product degradation. As far as the authors are aware, this is the only complex containing two metalated iminophosphine ligands as well as the only instance of a six-membered metallacycle formed from metalation of this iminophosphine ligand.

When bis(cycloocta-1,5-diene)platinum was reacted with a, the tris(phosphine) complex $[Pt(P)_3]$ (12a) was formed along with the hydride complex 9a. The new complex displayed a single

Scheme 5^{*a*}



resonance at 42.4 ppm in the ³¹P NMR spectrum with ¹ J_{PtP} = 4420 Hz. The chemical shift and coupling constant were consistent with the ³¹P NMR data of [Pt(PPh₃)₃]⁴⁵ and the tris(phosphine) complex [Pt(2-(PPh₂)C₆H₄CH=N((CH₂)₂C₆H₅))₃].²⁹ After two hours the NMR spectra of the reaction mixture showed the presence of unreacted ligand **a** and **9a** only. In contrast, when **b** and **c** were reacted in a similar manner with bis(cycloocta-1,5-diene)platinum, only the hydride complexes and unreacted ligand were observed.

In contrast to the reactions of the iminophosphine with $[Pt(nb)_3]$, the 1:2 reaction with the phosphinocarbonyl **d** did not proceed via the formation of detectable quantities of a hydride complex. Instead, reaction over 20 h led to the observation of an intermediate norborn-2-yl complex of platinum **13d**, formed by the migration of the aldehyde hydrogen to

Scheme 6^a



^{*a*} Ar = $C_6H_4CH=O$.



Figure 4. ORTEP diagram of *cis*-**6d** \cdot C₆H₆ showing 50% probability thermal ellipsoids. H-atoms have been omitted for clarity. Occupancy of O(1a) and O(1b) is 47% and 53%, respectively.

coordinated norbornene with the concomitant formation of a five-membered metallacycle (Scheme 6). In agreement with the proposed structure of the intermediate, both values of ${}^{1}J_{PtP}$ (1696 and 1642 Hz) are typical of ${}^{31}P$ *trans* to carbon. Conversion of **13d** to **6d** occurs through the elimination of norbornene and hydrogen gas, the latter observed as a sharp singlet in the ${}^{1}H$ NMR spectrum at 4.62 ppm (in CDCl₃). Over a period of several days at room temperature orange-red and colorless crystals of respectively the *cis-* and *trans*-bis-chelate complexes **6d** form.

The X-ray crystal structure of $cis-6d \cdot C_6H_6$, isolated as a benzene solvate in space group C2/c, confirms the structural predictions based on the NMR data (Figure 4). Details of the structural solution and refinement are given in Table 2, and selected bond lengths and angles are given in Table 5. The platinum atom lies on a crystallographic C_2 axis and is coordinated to two phosphorus atoms and to the two carbonyl carbons. The nine atoms comprising the bis-chelate core of the molecule are substantially coplanar, as are the attached phenyl rings. The two oxygen atoms are bent out of the plane of the rings quite noticeably, probably as a result of strong repulsive interactions (apparent O–O separation 264 pm; sum of van der Waals radii 304 pm). However, there are significant anisotropic thermal parameters associated with the oxygen atoms, suggesting that their true position is not precisely defined by the refinement. A

Table 5. Selected Bond Distances (Å) and Angles (deg) for cis-6d \cdot C₆H₆

Pt(1)-P(1) Pt(1)-C(1) P(1)-C(3)	2.3096(12) 2.073(5)	C(1)-C(2) C(1)-O(1A) C(1) - O(1B)	1.495(8) 1.333(15) 1.209(17)
P(1)-P(1)-P(1) P(1)-P(1)-P(1) C(3)-P(1)-C(10)	104.45(6) 106.1(2)	C(1) - O(1B) C(1) - Pt(1) - C(1)	83.16(17)

Scheme 7



disordered model in which one oxygen lies close to the plane and the other is displaced from the plane by 0.64 Å refines well.

From the molecular structure it can be seen that there is the potential for the two carbonyl oxygen atoms in *cis*-**6d** to coordinate to another center. Reaction of *cis*-**6d** with the hydrocarbon acid CH₂(SO₂CF₃)₂ confirmed this, forming the protonated complex **6d**+**H**⁺, where the proton is bound to the two oxygens (Scheme 7). In the ¹H NMR spectrum of this complex the shared proton appears at 22.05 ppm with ³*J*_{PtH} = 104.2 Hz, indicating the proton is strongly bound.⁴⁶ While the signal in the ³¹P NMR spectrum has not shifted significantly (δ = 45.2 ppm), the ¹*J*_{PtP} has increased (2114 Hz as opposed to 1843 Hz in the parent compound). The ability of metalla- β -diketones of the type [(CO)_{*x*}M(RCO)(R'CO)]⁻ to coordinate Lewis acids through two carbonyl moieties has been investigated by Lukehart.³⁸ Garralda and co-workers have extensively investigated the coordination chemistry of irida- β -diketones.³⁷

It is well known that the hydrogen atoms on a carbon in the α -position to a carbonyl are particularly reactive, for example, in keto-enol tautomerism. This proved to be the case when e was reacted with Pt(0) reagents. Thus the reaction of ketophosphine **e** with $[Pt(nb)_3]$ (2:1) in C₆D₆ at 20 °C under a nitrogen atmosphere initially afforded a mixture of the mono- and bisnorbornene complexes 8e and 7e in the presence of excess ligand (Scheme 8). Interestingly, this reaction proceeded through the short-lived hydride complex 9e, analogous to that seen in the iminophosphine reactions, rather than a norbornyl intermediate as d does. Over two days a new complex forms with two phosphine ligands that show very different chemical shifts (19.2 and 41.0 ppm, J_{PP} = 8.1 Hz). This is indicative of the presence of both five- and six-membered metallacyclic rings.³⁶ The observation of a signal in the ¹H NMR spectrum at 2.19 ppm with ¹⁹⁵Pt satellites ascribed to a methyl group and a broad signal at 6.06 ppm assigned to a hydroxyl proton (confirmed by the addition of D_2O) suggests that this complex is the 5,6-bis-metallacycle 14e. The partial reduction of the ketone function is achieved by the hydride ligand that results from the metalation of the other ligand to afford the six-membered metallacycle. The magnitude of ${}^{1}J_{\text{PtP}}$ for both phosphorus nuclei suggests they are cis to each other (Table 1).

Scheme 8^a



When the same reaction is carried out in air, the major product was *cis* and *trans* isomers of the bis-chelate **6e**. These are readily distinguished by the different magnitudes of ${}^{1}J_{PtP}$. Furthermore, if a solution of the *cis-5,6*-complex **14e** is stirred in air, the ligand that forms the five-membered ring rearranges, with the loss of two hydrogen atoms, to form a second six-membered metallacycle.

In this work three different coordination modes have been observed when the iminophosphine ligands react with platinum. Bidentate $P_{,N}$ binding was observed with platinum(II), while both monodentate P coordination and the formation of a P,C chelate were observed in the reactions with Pt(0) starting materials. These results provide support for the proposal that these ligands would display hemilabile behavior in platinum catalysts going through 0 and +2 oxidation states. However, the propensity to form stable P,C metallacyclic complexes could severely limit catalyst lifetimes. In contrast, while a larger number of coordination modes has been previously reported for the phosphinocarbonyl ligands, only two modes of coordination were observed in this research. Formation of a P,C chelate through oxidative addition was observed with both Pt(II) and Pt(0), as was coordination through the phosphorus alone. We have also observed that the chelate-assisted oxidative addition of a C-H bond in these ligands occurs more readily for the phosphinocarbonyl ligands than for the iminophosphines.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out using degassed solvents and standard Schlenk techniques under a nitrogen atmosphere unless stated otherwise. The starting materials used in this work were obtained from Sigma-Aldrich except 2-fluoroacetophenone which was obtained from Merck. The two iminophosphine ligands, a and b,¹² 2-diphenylphosphinobenzaldehyde, d,⁴⁷ 2-diphenylphosphinoacetophenone, e,⁴⁸ dichloro(hexa-1,5-diene)platinum,⁴⁹ diethyl(cycloocta-1,5-diene)platinum,⁵⁰ bis(cycloocta-1,5-diene)platinum,⁵¹ and bis(trifluoromethylsulfonyl)methane⁵² were synthesized using standard literature methods. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled under a nitrogen atmosphere from sodium benzophenone ketyl immediately prior to use. All other solvents used were of analytical grade and dried over molecular sieves. Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Unity Inova spectrometer

operating at 300 and 121 MHz for ¹H and ³¹P spectra, respectively, a Varian Unity Inova spectrometer operating at 500, 125, and 202 MHz for ¹H, ¹³C, and ³¹P spectra, respectively, and a Varian DirectDrive spectrometer operating at 600 and 61 MHz for ¹H and ¹⁵N spectra, respectively. NMR spectra were recorded in deuterated benzene (C_6D_6) , unless stated otherwise. All direct-detected ¹H and ¹³C chemical shifts, δ (ppm), were referenced to the residual solvent peak of the deuterated solvent.⁵³ Indirectly detected ¹⁵N shifts were referenced to the unified TMS scale with a Ξ ratio of 10.136767. 54 $^{31}\mathrm{P}$ NMR spectra were measured with ¹H-decoupling and referenced to 85% H₃PO₄. Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrophotometer (resolution 4 cm⁻¹) in absorbance mode, using pressed KBr discs. All spectral data were obtained at ambient temperature, unless otherwise stated. Elemental analysis was performed at the Campbell Microanalytical Laboratory at Otago University, Dunedin. Electrospray ionization mass spectroscopy was performed by the GlycoSyn QC laboratory at Industrial Research Limited, using a Waters Q-TOF Premier Tandem mass spectrometer.

Synthesis of Iminophosphine Ligand 2-(PPh₂)C₆H₄C-(CH₃)=N(2,6-Me₂C₆H₃), c. This synthesis is based on the synthesis of 2-(PPh₂)C₆H₄C(CH₃)=N(2,6-ⁱPr₂C₆H₃).⁵⁵ Titanium tetrachloride (3 mL, 1 mol L⁻¹ in toluene, 3 mmol) was slowly added to a solution of 2-fluoroacetophenone (0.8 mL, 6.25 mmol) and 2,6-dimethylaniline (2 mL, 14.8 mmol) in toluene (4 mL) at 0 °C. The resulting solution was allowed to warm to room temperature and stirred overnight. The suspension was filtered through alumina and rinsed with ethyl acetate. The filtrate was concentrated to an oil. As NMR spectra of the oil showed that the reaction had not gone to completion, this oil was dissolved in toluene (4 mL), and 2,6-dimethylaniline (2 mL, 14.8 mmol) was added. The solution was cooled to 0 °C, and TiCl₄ (3 mL, 1 mol L⁻¹ in toluene, 3 mmol) was added. The resulting suspension was allowed to warm to room temperature and stirred overnight. The reaction mixture was purified in the same manner as above to yield the desired imine as a dark green oil (0.848 g, 56%).

A solution of this imine in Et_2O (5 mL) was added to a solution of potassium diphenylphosphide in THF. After stirring at room temperature for three hours ethyl acetate and water (5 mL each) were added. The aqueous layer was removed, and the organic layer was washed with brine (2 × 5 mL), dried over magnesium sulfate, filtered, and concentrated to a yellow oil. The crude product was purified by flash chromatography (5% ethyl acetate in hexane) to give the iminophosphine **c** as a yellow oil, which crystallized over two days (0.619 g, 24%).

¹H NMR: δ/ppm 7.45 (ddd, 7.8, 4.5, 1.3 Hz, 1H, Ar-H), 7.38–7.29 (m, 5H, Ar-H), 7.07 (td, 7.8, 1.3 Hz, 1H, Ar-H), 7.02–6.86 (m, 10H, Ar-H), 1.90 (s, 6H, 2 × Ar-CH₃), 1.77 (d, J_{PH} = 1.5 Hz, 3H, CH₃). ¹³C NMR: δ/ppm 164.0 (s, C=N), 148.2 (s, Ar-C), 143.3 (d, J_{PC} = 17.1 Hz, Ar-C), 140.7 (d, J_{PC} = 10.5 Hz, Ar-C), 139.1 (d, J_{PC} = 22.5 Hz, Ar-C), 135.9 (s, Ar-C), 134.1 (d, J_{PC} = 20.0 Hz, Ar-C), 129.4 (s, Ar-C), 128.9 (d, J_{PC} = 2.9 Hz, Ar-C), 128.6 (d, J_{PC} = 6.6 Hz, Ar-C), 128.4 (s, Ar-C), 128.1 (s, Ar-C), 128.0 (s, Ar-C), 126.3 (s, Ar-C), 123.2 (s, Ar-C), 18.6 (d, J_{PC} = 1.9 Hz, CH₃), 18.5 (d, J_{PC} = 5.8 Hz, Ar-CH₃). ³¹P NMR: δ/ppm -9.3 (s). ¹⁵N NMR: δ/ppm -31.0 (s). IR: ν_{max}/cm^{-1} 1654 (C=N stretch). Analysis: C, 82.5; H, 6.5; N, 3.4 (C₂₈H₂₆NP requires C, 82.5; H, 6.4; N, 3.4).

Synthesis of Dimethyl(hexa-1,5-diene)platinum. Dichloro-(hexa-1,5-diene)platinum (0.348 g, 1.0 mmol, finely powdered) was suspended in dry Et_2O (5 mL). A solution of dimethylzinc (2 mL, 1 mol L⁻¹ in toluene, 2 mmol) was added over 10 min. The mixture was stirred until the last crystals of the starting material had dissolved. A solution of ammonium chloride in water was added, and the mixture was stirred for 30 min. The organic layer was decanted, and the aqueous layer was extracted with Et_2O (5 mL). The organic fractions were combined and dried over anhydrous sodium sulfate. The solvent was evaporated, leaving a pale oil, which crystallized slowly. The crude product was sublimed at 50 °C and ~0.5 mmHg, affording white crystals (0.260 g, 85%). ¹H NMR: δ/ppm 4.47 (m, 2H, 2 × =CH), 4.08 (d, 7.8, J_{PtH} = 39 Hz, 2H, =CH₂), 3.19 (q, 16.0 Hz, 2H, =CH₂), 1.76 (m, 2H, CH₂), 1.57 (m, 2H, CH₂), 1.21 (s, J_{PtH} = 84 Hz, 6H, 2 × Pt-CH₃). ¹³C NMR: δ/ ppm 102.9 (s, J_{PtC} = 44 Hz, =CH), 82.8 (s, J_{PtC} = 42 Hz, =CH₂), 30.7 (s, J_{PtC} = 9 Hz, CH₂), 9.9 (s, J_{PtC} = 798 Hz, Pt-CH₃). IR: ν_{max}/cm^{-1} 3075, 3018 (sp² C-H stretch), 2932, 2872 (sp³ C-H stretch), 956, 934 (alkene C-H bending). Analysis: C, 31.5; H, 5.4 (C₈H₁₆Pt requires C, 31.3; H, 5.3).

Synthesis of Tris(norbornene)platinum. The synthesis of tris(norbornene)platinum reported here is based on the synthesis of tris(styrene)platinum using a silane-reducing agent.⁵⁶ Dichloro(hexa-1,5-diene)platinum (10 g, 29 mmol, finely powdered) was added to a stirred solution of norbornene (24 g, 260 mmol) in diethyl ether (50 mL), followed by 2 mL of triethylsilane. The mixture was stirred at room temperature for 30 min, after which a further 10 mL of triethylsilane was added in 1 mL portions over one hour. At each addition of silane, the temperature of the solution rose and a faint yellow color appeared, which then slowly disappeared as the reaction proceeded. The solution was saturated with product at \sim 30 °C, and masses of fine crystals formed if the solution became too cold. The reaction flask was cooled to 4 °C overnight and then to -20 °C for a further day to complete crystallization. The crystals were filtered at -5 °C, washed with cold hexane (3 × 5 mL), and dried under vacuum for a short period (11.7 g, 84%).

The reaction produces byproduct that are solid at low temperature. These may co-crystallize with tris(norbornene)platinum if a second or third crop of crystals is sought. The product was purified by dissolving in hexane along with a small crystal of norbornene, passing the solution through a short column of alumina, and recrystallizing at low temperature. Tris(norbornene)platinum crystallizes as fine white needles that entrain the solvent in the mat of crystals. Slow crystallization affords larger crystals that are easier to wash and dry. The NMR spectra of the crystals formed were identical to those of samples produced by other methods.⁵¹

Reactions with Platinum(II) Complexes. *Example Method for Synthesis of Platinum(II) Complexes of Iminophosphine Ligands.* Diethyl(cycloocta-1,5-diene)platinum (47 mg, 0.13 mmol) and ligand a (0.13 mmol) were combined in a Schlenk tube and dissolved in diethyl ether (10 mL). The reaction was stirred at ambient temperature, and after four hours the solution had turned dark orange. Orange crystals suitable for single-crystal X-ray structure determination of 2a were grown from the reaction mixture at ambient temperature. The complex was isolated by filtration (62 mg, 74%). (See Supporting Information for the details of the synthesis of 1a-3c.)

Reaction of Dimethyl(hexa-1,5-diene)platinum with Ligand **d**. Dimethyl(hexa-1,5-diene)platinum (20 mg, 0.07 mmol) was dissolved in CDCl₃ (0.5 mL) in an NMR tube. Ligand **d** (39 mg, 0.13 mmol) was added to the solution, rapidly forming complex 4d. The chelation of one diphenylphosphinobenzaldehyde ligand to platinum followed, producing 5d. This complex was recrystallized from the inward diffusion of Et₂O into CH₂Cl₂, yielding orange crystals (42 mg, 80%).

5d · CH₂Cl₂. IR: ν_{max} /cm⁻¹ 1694 (C=O stretch, pendant CHO), 1618 (C=O stretch, coordinated C=O). Analysis: C, 54.4, H, 3.9 (C₃₉H₃₂O₂P₂Pt·CH₂Cl₂ requires C, 54.9; H, 3.9).

Reaction of Dimethyl(hexa-1,5-diene)platinum with Ligand **d**: Synthesis of **6d**. Dimethyl(hexa-1,5-diene)platinum (80 mg, 0.261 mmol) and ligand **d** (165 mg, 0.569 mmol) were combined in a twonecked flask, and toluene (20 mL) was added. The mixture was stirred at room temperature for 16 h followed by reflux for 16 h. A microcrystalline solid, containing mostly *cis*-**6d** and some *trans* isomer, precipitated from the solution. The mixture was cooled and filtered through sintered glass. The solid was washed with cold toluene and then hexane (143 mg, 71%). Pure *cis*-**6d** can be isolated by reacting the crude material containing *cis* and *trans* isomers with tetrafluoroboric acid or $CH_2(SO_2CF_3)_2$ in dichloromethane to protonate the *cis* isomer exclusively. The *trans* isomer can then be removed via filtration. The *cis* isomer can then be deprotonated with DABCO or NaH to yield a pure sample of *cis*-**6d**.

cis-6d. IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 1632 (C=O stretch).

Protonation of Complex **6d**: Synthesis of **6d+H⁺**. Complex *cis*-6d (27.7 mg, 0.0358 mmol) was suspended in CH_2Cl_2 (10 mL), and $CHPh(SO_2CF_3)_2$ (10.0 mg, 0.0358 mmol) was added. An immediate color change from red to yellow was observed along with the complete dissolution of all solid **6d**. The solvent was removed under vacuum, and the product was recrystallized from CH_2Cl_2 and Et_2O , forming yellow, needle-shaped crystals (27.2 mg, 72%).

6d+H⁺. IR: ν_{max} /cm⁻¹ 1524 (C=O stretch). Analysis: C, 49.4, H, 3.2 (C₄₇H₃₄F₆O₆P₂PtS₂ requires C, 49.9; H, 3.0).

Reaction of Dimethyl(hexa-1,5-diene)platinum with Ligand **e**. Dimethyl(hexa-1,5-diene)platinum (80 mg, 0.26 mmol) and ligand **e** (170 mg, 0.56 mmol) were added to a Schlenk tube. The solids were dissolved in CH_2Cl_2 (5 mL, degassed). The immediate formation of **4e** was quickly followed by the chelation of one of the ligands to form **5e**.

Reaction of Dimethyl(hexa-1,5-diene)platinum with Ligand e: Synthesis of cis-**6e**. Dimethyl(hexa-1,5-diene)platinum (80 mg, 0.261 mmol) and ligand e (165 mg, 0.543 mmol) were dissolved in CHCl₃ and refluxed for 72 h. The solvent was removed under vacuum, and the solid was washed with toluene. The white microcrystalline solid was dissolved in a minimum of CH₂Cl₂ and recrystallized by inward diffusion of Et₂O. This method produced exclusively the *cis* isomer.

cis-**6e**. IR: v_{max}/cm^{-1} 1629 (C=O stretch). HRMS: calcd for C₄₀H₃₃O₂P₂Pt [M + H]⁺ m/z = 801.1583; found 801.1580. Analysis: C, 60.2; H, 4.1 (C₄₀H₃₃O₂P₂Pt requires C, 59.9; H: 4.0).

Reactions with Platinum(0) Complexes. *Reactions of Tris*-(*norbornene*)*platinum(0) with Ligand* **a** or **b**. Tris(norbornene)*platinum* and ligand **a** or **b** were reacted in a 1:1, 1:2, and 1:3 ratio. These syntheses were carried out using 30 mg of tris(norbornene)*platinum* (0.063 mmol) and the appropriate amount of ligand. The two solids were combined in an NMR tube and dissolved in C_6D_6 (0.5 mL). The recorded ¹H and ³¹P NMR spectra initially showed the formation of complexes 7a and 8a or 7b and 8b. After one day, the ¹H and ³¹P NMR spectra showed the formation of complex 9a or 9b.

Reactions of Tris(norbornene)platinum(0) with Ligand **c**. Tris-(norbornene)platinum and ligand **c** were reacted in a 1:1, 1:2, and 1:3 ratio. These reactions were carried out using 28 mg of tris(norbornene)platinum (0.059 mmol) and the appropriate amount of ligand. The two solids were combined in an NMR tube and dissolved in C_6D_6 (0.5 mL). The recorded ¹H and ³¹P NMR spectra initially showed the formation of complex 7**c** and an extremely small amount of 8**c**. While the ¹H and ³¹P NMR spectra recorded after one hour showed the formation of complex 9**c**, the ¹H and ³¹P NMR spectra recorded after one day showed the formation of a small amount of *cis*-6**c**. If the reaction is left at room temperature over time, the amount of *cis*-6**c** increases and a detectable amount of *trans*-6**c** is formed. However, the reaction never goes to completion.

Reaction of Tris(ethene)platinum(0) with Ligand **c**: Synthesis of Complexes **10c**, **11c**, and **6c**. Under an atmosphere of ethene, tris-(ethene)platinum (22 mg, 0.079 mmol) and ligand **c** (64 mg, 0.158 mmol) were combined in an NMR tube and dissolved in C_6D_6 (0.5 mL). The ¹H and ³¹P NMR spectra recorded initially showed the formation of both **10c** and **11c**. After one day, there was only **11c** present. Nitrogen was bubbled through the sample to convert **11c** to **9c**. The sample was then heated at 40 °C for five days to give both the *cis* and *trans* isomers of the 6,6-metallacycle **6c**. The *cis* isomer was the major product. The solution was filtered through alumina and washed with hexane and toluene to give a sample of the two isomers pure enough for spectroscopy but not elemental analysis.

Reaction of Bis(cycloocta-1,5-diene)platinum(0) with Ligand **a**, **b**, *or* **c**. Bis(cycloocta-1,5-diene)platinum (13 mg, 0.031 mmol) and ligand **a**, **b**, or **c** (0.093 mmol) were combined in an NMR tube and dissolved

NMR spectra. *Reaction of Bis(cycloocta-1,5-diene)platinum(0) with Ligand* **b**. Bis(cycloocta-1,5-diene)platinum (53 mg, 0.13 mmol) and ligand **b** (117 mg, 0.26 mmol) were dissolved in hexane (5 mL) to produce **9b**, which precipitated as a yellow powder. The yellow powder was dissolved in Et₂O with a drop of cycloocta-1,5-diene. Yellow block crystals suitable for single-crystal X-ray structure determination were obtained from inward diffusion of hexane at 4 °C.

Reaction of Tris(norbornene)platinum(0) with Ligand **d**. Tris-(norbornene)platinum (100 mg, 0.21 mmol) and ligand **d** (128 mg, 0.44 mmol) were combined in a Schlenk tube. Toluene (7 mL, dry, degassed) was added, and the mixture was stirred and then left to stand for 20 h. Yellow crystals formed. The solvent was removed under vacuum, and the residue was dried under vacuum for two hours to remove free norbornene. NMR analysis showed a virtually pure sample of 13d, although in solution the complex reacts to form *cis*-6d. After one week at room temperature, orange crystals of *cis*-6d·C₆H₆ suitable for singlecrystal X-ray structure determination grew out of the reaction mixture.

13d. HRMS: calculated for $C_{45}H_{41}O_2P_2Pt^+$ $[M + H]^+ m/z = 869.2209$; found 869.2211. Analysis: C, 62.7; H, 4.8 ($C_{45}H_{40}O_2P_2Pt$ requires C, 62.1; H, 4.6).

Reaction of Tris(norbornene)platinum(0) with Ligand e in Air: Synthesis of 6,6-Metallacycle 6e. Tris(norbornene)platinum (50 mg, 0.10 mmol) and ligand e (64 mg, 0.20 mmol) were combined in a flask and dissolved in toluene (10 mL). The flask was left open to air in a fumehood, and over five days white, block-like crystals formed. While complexes 7e and 8e are formed as intermediates, this reaction ultimately forms 6e as the major product. The crystals were separated from the supernatant and washed with hexane. Both the *cis* and *trans* isomers of 6e were formed with the crystals of the *cis* isomer needle-like in shape and the *trans* isomer plate-like.

trans-**6e**. IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 1629 (C=O stretch). HRMS: calcd for C₄₀H₃₃O₂P₂Pt [M + H]⁺ m/z = 801.1583; found 801.1580. Analysis: C, 60.2; H, 4.1 (C₄₀H₃₃O₂P₂Pt requires C, 59.9; H: 4.0).

Reaction of Tris(norbornene)platinum(0) with Ligand *e* under Nitrogen: Synthesis of 5,6-Metallacycle **14e**. Tris(norbornene)platinum (59 mg, 0.124 mmol) and ligand *e* (75 mg, 0.248 mmol) were added to a Schlenk tube. CH₂Cl₂ (3 mL) was added, and the mixture was stirred overnight at room temperature. This reaction forms **7e** and **8e** first before forming the short-lived hydride complex **9e**, which rapidly converts into **14e**. The solvent and residual norbornene were removed under vacuum, leaving yellow solid **14e**. The product is sensitive to oxygen in solution and converts to **6e** over time.

X-ray Structure Analysis. Orange crystals of **2a** were obtained by recrystallization from Et₂O. Orange crystals of *cis*-**6d** \cdot C₆H₆ were obtained from the reaction of tris(norbornene)platinum and **d** in benzene. Yellow block crystals of **9b** were obtained from the slow diffusion of hexane into a Et₂O solution of **9b** in the presence of a small amount of cycloocta-1,5-diene. X-ray diffraction data were collected on a Bruker SMART CCD diffractometer using Mo K α radiation. Data were reduced using Bruker SAINT software. Absorption correction was performed using the SA-DABS program. The structures of **2a** and *cis*-**6d** \cdot C₆H₆ were solved using Patterson methods, and **9b** was solved using direct methods using SHELXS97 and refined using SHELXL97.⁵⁷

ASSOCIATED CONTENT

Supporting Information. Details of the synthesis of 1a-3c, ¹H, ¹³C, ¹⁵N, and ³¹P NMR data for all of the platinum

complexes, and X-ray crystallographic files in CIF format for 2a, *cis*- $6d \cdot C_6H_6$, and 9b. This material is available free of charge via the Internet at http://pubs.acs.org.

ARTICLE

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