Unusually Stable Four-Membered Chelate Rings in Nickel(II), Palladium(II), and Platinum(II) Complexes with the Ligand 2,2-Bis(diphenylphosphino)propane (2,2-dppp). Crystal and Molecular Structure of $[PdI_2(2,2\text{-dppp})]\cdot 0.8CH_2Cl_2$

Jim Barkley, Melanie Ellis, Simon J. Higgins,* and Mark K. McCart

Department of Chemistry, Chemistry Buildings, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom

Received October 28, 1997

The ligand $Ph_2PC(CH_3)_2PPh_2$ (2,2-dppp) reacts with Ni(II) salts to give robust square-planar chelate complexes $[NiX_2(2,2\text{-dppp-}P,P')]$ (X = Cl, **1**; X = Br, **2**) and the salt $[Ni(2,2\text{-dppp})_2](ClO_4)_2$ (**3**). The Pd(II) analogues $[PdCl_2(2,2\text{-dppp})]$ (**4**), $[PdI_2(2,2\text{-dppp})]$ (**5**), and $[Pd(2,2\text{-dppp})_2](BF_4)_2$ (**6**) have also been made. The crystal structure of **5** (obtained as $\mathbf{5}\cdot 0.8CH_2Cl_2$) has been determined by X-ray diffraction. The geminal $C(CH_3)_2$ group, when compared with related $Ph_2PCH_2PPh_2$ (dppm) complexes, causes a small compression of the P−C−P chelate ring angle (to 91.3(3)° for **5**). With $[PtCl_2(PhCN)_2]$, 2,2-dppp affords $[PtCl_2(2,2\text{-dppp})]$ (**7**), which undergoes metathesis with NaI to give $[PtI_2(2,2\text{-dppp})]$ (**8**), and $[Pt(2,2\text{-dppp})_2]Cl_2$ (**9**) was obtained by reaction of $[PtCl_2(PhCN)_2]$ with 2 equiv of 2,2-dppp. Reactions were then attempted with **7** and **9**, which are known to result in ring-opening reactions with the corresponding complexes of dppm, but in all cases, only 2,2-dppp chelate complexes could be isolated. Thus, treatment of **7** or **9** with excess MeLi gave exclusively $[PtMe_2(2,2\text{-dppp})]$ (**10**) rather than *cis,cis*-$[Pt_2Me_4(2,2\text{-dppp})_2]$. Attempts to ring-open **10** with excess 2,2-dppp to give *cis*-$[PtMe_2(2,2\text{-dppp}-P)_2]$ were unsuccessful. Treatment of **10** with 1 equiv of HCl or, better, treatment of [PtCl(Me)(1,5-cyclooctadiene)] with 2,2-dppp gave only mononuclear [PtCl(Me)(2,2-dppp)] (**11**) and no dimer of the type $[MePt(\mu\text{-}2,2\text{-dppp})_2(\mu\text{-Cl})PtMe]Cl$. Treatment of **7** with 2 equiv of NaCN in EtOH gave the chelate complex $[Pt(CN)_2(2,2\text{-dppp})]$ (**12**) rather than *trans,trans*-$[Pt_2(CN)_4(\mu\text{-}2,2\text{-dppp})_2]$, and treatment of **7** with LiC≡CPh in thf or (better) $H_2NNH_2\cdot H_2O$/HC≡CPh in EtOH gave $[Pt(C{\equiv}CPh)_2(2,2\text{-dppp})]$ (**13**), rather than *trans,trans*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-}2,2\text{-dppp})_2]$. Reaction of **7** with $LiC{\equiv}CBu^n$ in thf likewise gave $[Pt(C{\equiv}CBu^n)_2(2,2\text{-dppp})]$ (**14**) in low yield. The complexes were characterized by microanalyses (C, H, N and, in some cases, halide), infrared spectroscopy, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, and fast atom bombardment mass spectrometry.

The coordination chemistry of ligands R_2PXPR_2 (R = alkyl, alkoxy, aryl; X = CH_2, NH, NR, O) has been extensively investigated. The archetypal example $Ph_2PCH_2PPh_2$ (dppm) can chelate, but because of the strain inherent in a four-membered chelate ring it can also form η^1 complexes or bridge two metal atoms in a variety of coordination geometries.[1,2] There is often a fine balance between these types of behaviors. For example, both *cis,cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$ and $[PtMe_2(\text{dppm-}P,P')]$ may be prepared (the chelate is the thermodynamically stable form),[3] and in solution at high concentrations and low temperatures, $[PtMe_2(\text{dppm-}P)_2]$ can be generated from $[PtMe_2(\text{dppm-}P,P')]$ and dppm.[4] Routes to heterobimetallic complexes bridged by dppm have been developed exploiting the tendency of mononuclear complexes M(dppm-*P*)$_n$ or M(dppm-*P*,*P*′)$_n$ to react with a labile source of a second metal ion to afford the species $M(\mu\text{-dppm})_nM'$,[2,5,6] most notably by Shaw's group.[4,7−11]

It is clear that varying R in ligands $R_2PCH_2PR_2$ causes very significant changes in their coordination chemistry. Whereas the ligand $Me_2PCH_2PMe_2$ has a greater tendency to bridge two metal centers than does $Ph_2PCH_2PPh_2$,[2,12] the use of bulkier alkyl substituents

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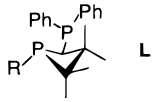
S0276-7333(97)00941-2 CCC: $15.00
Publication on Web 03/31/1998

leads to ligands which are highly effective chelates and which promote some very unusual coordination chemistry and homogeneous catalysis. For example, *cis* hydrido alkyl complexes of Pt(II) are normally very unstable with respect to reductive elimination of alkane, but the complex [Pt(H)(^{i}Pr)(^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)] can be isolated, in which both the *cis* hydrido alkyl arrangement and the four-membered chelate ring are stabilized by the bulky exocyclic ^{t}Bu groups.[13] Further, on photolysis, this complex eliminates propane to give an intermediate, postulated as the "bent", 14 e$^-$ [Pt(^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)], which can oxidatively add C−H bonds,[13] and even C−F bonds,[14] or coordinate alkenes to give the stable complexes [Pt(^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)(η^2-alkene)].

Quite early in the development of dppm coordination chemistry it was suggested that substitution at the methylene carbon would have little effect on the coordination chemistry of ligands R$_2$PCR′$_2$PR$_2$ (R = alkyl, aryl; R′ = H, alkyl).[15] Although this conclusion was based upon few examples, remarkably little work on this topic has been reported since. The ligand 1,1-bis(diphenylphosphino)ethane (1,1-dppe) does appear largely to mimic dppm in its coordination chemistry. For example, with [Rh$_2$Cl$_2$(CO)$_4$], both ligands react to give the dimers *trans*-[Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$][16,17] and [Rh$_2$(μ-Cl)(CO)$_2$(μ-1,1-dppe)$_2$]Cl,[18] respectively. Additional steric effects may be responsible for the formation of the chloride-bridged salt in the latter case; interestingly, the unusual chiral 1,1-diphosphine ligand **L** gives a very similar dimer, [Rh$_2$(μ-Cl)(CO)$_2$(μ−**L**)$_2$]Cl, on treatment with [Rh(COD)Cl]$_2$ (COD = cycloocta-1,5-diene) and CO.[19]



L

(R = menthyl)

Similar "A-frame" complexes [Pd$_2$Cl$_2$(μ-diphosphine)$_2$(μ-C=CH$_2$)] are obtained on treatment of [Pd(PPh$_3$)$_4$] with Cl$_2$C=CH$_2$ and either dppm or 1,1-dppe in refluxing benzene,[20] and both [Pd$_2$Cl$_2$(μ-dppm)$_2$](*Pd*−*Pd*) and [Pd$_2$Cl$_2$(μ-1,1-dppe)$_2$](*Pd*−*Pd*) have been synthesized by conproportionation of labile Pd^0 and Pd^{II} starting materials in the presence of dppm or 1,1-dppe.[21] The addition of nucleophiles to the double bond of chelated (Ph$_2$P)$_2$C=CH$_2$ has been demonstrated as a route to coordinated, functionalized diphosphines of the type (Ph$_2$P)$_2$CHCH$_2$X (*X* = −NHR, −NR$_2$, −OR, −C≡CR, etc.),[22−25] and we have used this reaction to prepare redox-active Ru^{II} complexes for oxide surface modification[26] and for incorporation into conjugated polymers.[27] However, little has so far been reported about the tendency of such complexes to undergo ring-opening reactions analogous to those of chelate complexes of dppm or 1,1-dppe.

Recently, we have shown that the ligand 2,2-bis(diphenylphosphino)propane (2,2-dppp) is very effective at chelating Rh(I), reacting with [Rh$_2$Cl$_2$(CO)$_4$] to give exclusively [RhCl(CO)(2,2-dppp-*P,P′*)], in marked contrast with both dppm and 1,1-dppe.[28] This work suggested that *complete* substitution by methyl groups for hydrogen at the methylene carbon greatly enhances the stability of four-membered chelate rings for 2,2-dppp over dppm or 1,1-dppe, in the same way that substitution of Bu^t for Ph groups at phosphorus appears to do in the chemistry of ^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$ compared with dppm. The effect is reminiscent of the Thorpe-Ingold (*gem*-dimethyl) effect in small organic ring systems, as pointed out by Shaw.[29] The remarkable chemistry observed with Pt group metal complexes of ^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$[13,14,30] has led us to begin investigating the coordination chemistry of 2,2-dppp with Ni(II), Pd(II), and Pt(II), and we report our initial results here.

Results and Discussion

Nickel and Palladium Complexes. Reaction of NiX$_2$·*n*H$_2$O in EtOH with 2,2-dppp gave, regardless of the stoichiometry employed, exclusively [NiX$_2$(2,2-dppp−*P,P′*)] (X = Cl, **1**; X = Br, **2**) as orange-red precipitates. These were characterized by (i) microanalyses (C, H), (ii) FAB mass spectrometry, which showed peaks corresponding to M$^+$ and (M − X)$^+$ for this formulation, with no higher mass peaks, (iii) the ^{31}P NMR spectra, which showed single, temperature-invariant, sharp resonances shifted upfield from the free ligand value, as expected for a four-membered diphosphine chelate ring,[4] in the same chemical shift range as the corresponding palladium complexes (below), and (iv) the ^{1}H NMR spectra, which showed triplets at 1.28 and 1.23 ppm, respectively, with $^3J_{PH}$ = 17.4 and 16.4 Hz, respectively.

Both **1** and **2** are robust in solution, and variable-temperature ^{31}P{^{1}H} spectroscopy shows no evidence for diphosphine ligand exchange reactions in solvents of different polarity (CH$_2$Cl$_2$, CH$_2$Cl$_2$/CH$_3$CN mixtures). These results contrast with the chemistry of dppm with Ni^{II}. In EtOH, dppm reacts with NiCl$_2$ to give exclusively [NiCl$_2$(dppm)$_2$] regardless of the stoichiometry employed.[31−33] Although a planar [NiCl$_2$(dppm-*P*)$_2$] structure was proposed on the basis of electronic

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spectra, it has since been shown that, at least in the solid state, "$[NiCl_2(dppm)_2]$" is five-coordinate $[NiCl_2(dppm\text{-}P,P')(dppm\text{-}P)]$.[34] A firm assignment of solution structure could not be made, although NMR and electronic spectral data were apparently not consistent with the solid-state structure being maintained in solution, and on recrystallization, $[NiCl_2(dppm\text{-}P,P')(dppm\text{-}P)]$ partially dissociates to $[NiCl_2(dppm\text{-}P,P')]$.[34] The latter may be isolated pure by combining $NiCl_2$ and dppm (1:1) in anhydrous, poorly coordinating solvents,[35] but it is labile.

The additional stability conferred on the chelate rings in **1** and **2** by the exocyclic *gem*-dimethyl group affects the potential of these complexes for catalysis. For the nickel−phosphine complex catalyzed cross-coupling of Grignard reagents with aryl halides, known as the Kumada coupling, $[NiX_2(Ph_2P(CH_2)_3PPh_2)]$ (X = Cl, Br) are the catalysts of choice. Neither $[NiCl_2(dppm)_2]$[36] nor $[NiCl_2(dppm)]$[37] act as catalysts for the coupling of Bu^nMgBr with C_6H_5Cl, the original test reaction for Kumada coupling.[36] We have shown in preliminary studies that complex **1** does catalyze this reaction,[37] with approximately the same activity and selectivity as for $[NiCl_2(dppe)]$.[36]

Treatment of an ethanol solution of $[Ni(H_2O)_6](ClO_4)_2$ with 2 equiv of 2,2-dppp afforded yellow $[Ni(2,2\text{-}dppp)_2](ClO_4)_2$ (**3**). The ^1H NMR spectrum of **3** showed a quintet at 1.76 ppm (apparent J_{PH} = 8.0 Hz), due to the geminal methyl groups, significantly downfield of the corresponding signals for **1** and **2**. The quintet pattern is caused by "virtual" coupling to all four ^{31}P nuclei; P−*trans*-P coupling constants in square-planar d^8 complexes are large.[38]

Treatment of $[PdCl_2(PhCN)_2]$ in CH_2Cl_2 with 2,2-dppp gave $[PdCl_2(2,2\text{-}dppp)]$ (**4**). Metathesis of this with NaI in acetone gave $[PdI_2(2,2\text{-}dppp)]$ (**5**); details and characterizing data are in the Experimental Section. The latter was also prepared in a one-pot reaction between $[\{Pd(OAc)_2\}_3]$, 2,2-dppp, and NaI in CH_2Cl_2/acetone. A one-pot reaction between $[PdCl_2(PhCN)_2]$, 2,2-dppp, and $AgBF_4$ in CH_2Cl_2/CH_3CN gave, after recrystallization, $[Pd(2,2\text{-}dppp)_2](BF_4)_2$ (**6**). Characterizing data are in the Experimental section; the FAB mass spectrum showed peaks due to $[M - BF_4]^+$ at 1017 amu and $[M - BF_4 - HBF_4]^+$ at 930 amu, respectively. As for the Ni^{II} salt **3**, the ^1H NMR spectrum of **6** (CD_3CN) showed a virtual quintet resonance due to the geminal methyl groups at 1.77 ppm (apparent J_{PH} = 8.8 Hz), significantly downfield of the resonances for **4** and **5**.

Crystal Structure of $[PdI_2(2,2\text{-}dppp)]\cdot 2CH_2Cl_2$. Crystals of **5** suitable for X-ray crystallography were obtained, as $[PdI_2(2,2\text{-}dppp)]\cdot 0.8CH_2Cl_2$, on recrystallization from CH_2Cl_2/MeOH. The molecular structure is shown in Figure 1, and selected bond lengths and angles are given in Table 1; experimental details are given in Table 2. The solvent molecules were distributed evenly between two sites within the asymmetric unit and were refined with occupancies of 0.4. The structure may be compared with those of $[PdI_2(\{Ph_2P\}_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3)]$,[23] $[PdI_2(dppm)]$[39] (for which bond length and angle data was accessed using the Cambridge

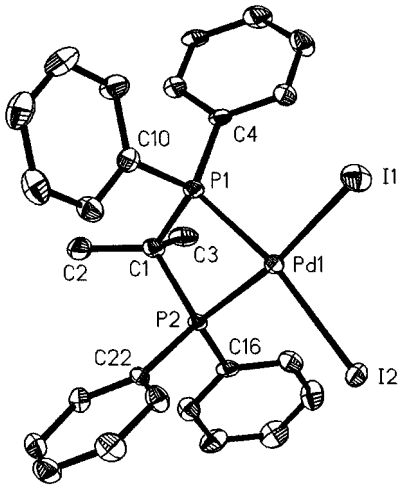

Figure 1. Molecular structure of $[PdI_2(2,2\text{-}dppp)]\cdot 0.8CH_2Cl_2$ (**5**). Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $5\cdot 0.8CH_2Cl_2$

Pd−I(1)	2.652(2)	P(1)−C(10)	1.808(6)
Pd−I(2)	2.643(1)	P(2)−C(1)	1.888(6)
Pd−P(1)	2.255(2)	P(2)−C(16)	1.818(6)
Pd−P(2)	2.247(2)	P(2)−C(22)	1.812(6)
P(1)−C(1)	1.894(6)	C(1)−C(2)	1.515(9)
P(1)−C(4)	1.805(6)	C(1)−C(3)	1.531(9)
I(1)−Pd−I(2)	93.12(5)	Pd−P(2)−C(1)	96.3(2)
I(1)−Pd−P(1)	99.24(7)	C(1)−P(2)−C(16)	108.6(3)
I(1)−Pd−P(2)	171.51(4)	C(1)−P(2)−C(22)	111.2(3)
I(2)−Pd−P(1)	167.64(4)	C(16)−P(2)−C(22)	108.5(3)
I(2)−Pd−P(2)	93.84(6)	P(1)−C(1)−P(2)	91.3(3)
P(1)−Pd−P(2)	73.84(7)	P(1)−C(1)−C(2)	117.4(4)
Pd−P(1)−C(1)	95.9(2)	P(1)−C(1)−C(3)	109.8(4)
C(1)−P(1)−C(4)	108.3(3)	P(2)−C(1)−C(2)	119.1(4)
C(1)−P(1)−C(10)	109.6(3)	P(2)−C(1)−C(3)	107.0(4)
C(4)−P(1)−C(10)	107.1(3)	C(2)−C(1)−C(3)	110.5(5)

Table 2. Data Collection, Structure Solution, and Refinement Parameters for $5\cdot 0.8CH_2Cl_2$

cryst habit	orange-yellow, needle
cryst dimens (mm)	0.20 × 0.15 × 0.35
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	10.705(7)
b (Å)	17.30(1)
c (Å)	16.707(9)
β (deg)	102.45(5)
V (Å^3)	3021(3)
calcd density (g/cm^3)	1.881
temp (K)	153 ± 1
μ(Mo Kα) (mm^{-1})	2.93
diffractometer	Rigaku AFC6S
θ range (deg)	0−25.0
no. of rflns collected	5700
no. of indep rflns (R_{int})	5389
ls params	313
$R(F)$, $R_w(F^2)$ ($F^2 > 3.0\sigma(F^2)$)[b]	0.032, 0.043

[a] Graphite-monochromated X-rays, wavelength 0.710 73 Å. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

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Structural Database[40] at the Chemical Database Service[41]), and $[PdCl_2(dppm)]$.[42] The metal−ligand bond distances are typical of members of this series. The only obvious effect of the geminal dimethyl moiety is to close up the P−C−P chelate ring angle slightly, from 93.9° for $[PdI_2(dppm)]$ and 93.0(1)° for $[PdCl_2(dppm)]$ to 91.3(3)° for **5**. There is no clear trend in the other chelate ring angles.

Platinum Complexes. Treatment of $[PtCl_2(PhCN)_2]$ with 1 equivalent of 2,2-dppp in CH_2Cl_2 gave $[PtCl_2(2,2\text{-dppp})]$ (**7**). The $^{31}P\{^1H\}$ NMR spectrum of **7** shows a singlet resonance, shifted upfield from the free ligand, with $^1J_{PtP} = 3135$ Hz. The upfield shift,[38] and the unusually low $^1J_{PtP}$ value for P−*trans*-Cl,[43] are both as expected for a four-membered chelate ring. In the ^1H NMR spectrum, the ligand methyl protons resonate as a triplet at 1.22 ppm ($^3J_{PH} = 17.2$ Hz). Any coupling to ^{195}Pt ($^4J_{PtH}$) is too small to be observed. Metathesis with NaI in acetone gave $[PtI_2(2,2\text{-dppp})]$ (**8**), characterized similarly. This complex was prepared earlier, by successive deprotonation of the ligand methylene group of $[PtI_2(dppm)]$ with $(Me_3Si)_2NLi$ and quenching with MeI.[44,45] Spectroscopically, it is very similar to **7**. Treatment of $[PtCl_2(PhCN)_2]$ with 2 equiv of 2,2-dppp in refluxing CH_2Cl_2/CH_3CN gave the salt $[Pt(2,2\text{-dppp})_2]Cl_2$ (**9**). The $^{31}P\{^1H\}$ NMR spectrum of **9** shows a singlet at −21.6 ppm, with $^1J_{PtP}$ typical of P−*trans*-P in four-membered chelate rings, 2268 Hz. In the ^1H NMR spectrum, the ligand methyl groups resonate as a second-order quintet at 1.80 ppm (apparent $J_{PH} = 8.4$ Hz); once again no ^{195}Pt coupling could be observed.

With complexes **7**−**9** in hand, we then carried out experiments known to result in ring opening with the analogous Pt^{II}−dppm complexes, to test the stability of the four-membered chelate rings formed by 2,2-dppp with Pt^{II}. We chose Pt^{II} complexes for the diagnostic value of $^1J_{PtP}$ couplings in the $^{31}P\{^1H\}$ NMR spectra.

Treatment of a thf suspension of **7** or **8** with excess MeLi gave exclusively $[PtMe_2(2,2\text{-dppp})]$ (**10**), in moderate yield. A better yield was obtained by the displacement of 1,5-cyclooctadiene (COD) from $[PtMe_2(COD)]$. That **10** is indeed the monomeric chelate complex is confirmed by the FAB mass spectrum, which shows clusters of peaks corresponding to $[M - Me]^+$ and $[M - Me - MeH]^+$ for this formulation (but no higher mass peaks), and the $^{31}P\{^1H\}$ NMR spectrum, which shows a singlet at −2.8 ppm, upfield from the free ligand, and a $^1J_{PtP}$ value of 1577 Hz, typical of a four-membered chelate diphosphine trans to methyl ligands.[4] The ^1H NMR spectrum showed a triplet centered at 1.29 ppm ($^3J_{PH} = 14.4$ Hz) due to the ligand methyl groups. There was no discernible $^4J_{PtH}$, although the corresponding $^3J_{PtH}$ values for the methylene protons of dppm in $[PtMe_2(dppm)]$ is 23.0 Hz.[4] A triplet at 0.83 ppm ($^3J_{PH}$ 6.7 Hz), with Pt satellites ($^2J_{PtH}$ 72.7 Hz), was assigned to the methyl ligands. This resonance is significantly upfield from the corresponding resonance for $[PtMe_2(dppm)]$ (1.00 ppm).[4]

When $[PtMe_2(dppm\text{-}P,P')]$ in chlorinated solvents is treated with excess dppm, an equilibrium is established with *cis*-$[PtMe_2(dppm\text{-}P)_2]$. The latter is favored by high concentration and low temperature and can be isolated as a pure solid.[4] However, when we treated a saturated (ca. 50 mM) solution of **10** in $CDCl_3/CH_2Cl_2$ with excess 2,2-dppp and monitored the $^{31}P\{^1H\}$ NMR spectrum at −60 °C, no trace of any species other than **10** and free 2,2-dppp could be detected. Also, whereas, depending upon starting materials and conditions, both $[PtMe_2(dppm\text{-}P,P')]$ and *cis,cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$ can be isolated,[3] we have been unable to make the 2,2-dppp analogue of the latter.

Treatment of **10** with 1 equiv of HCl in thf gave $[PtCl(Me)(2,2\text{-dppp-}P,P')]$ (**11**) exclusively. That **11** is mononuclear, with chelating 2,2-dppp, follows from the spectroscopic data. In particular, the $^{31}P\{^1H\}$ NMR spectrum shows an AX spin system to high field of the free ligand chemical shift, with Pt satellites for the two signals typical of P−*trans*-Cl and P−*trans*-Me. This contrasts with the behavior of $[PtMe_2(dppm\text{-}P,P')]$, which reacts with HCl in benzene to give the chloride-bridged "A-frame" complex $[MePt(\mu\text{-Cl})(\mu\text{-dppm})_2PtMe]Cl$.[46] A mixture of the latter and $[PtCl(Me)(dppm\text{-}P,P')]$ was obtained on treatment of $[PtCl(Me)(COD)]$ with dppm.[47] It was also observed earlier that for complexes with the formula $[PtCl(R)(dppm)]_n$, the chelate ($n = 1$) form is favored when R is bulky (e.g. $C_6H_2Me_3$-2,4,6) and the binuclear salt $[RPt(\mu\text{-Cl})(\mu\text{-dppm})_2PtR]Cl$ is favored when R = Me. For intermediate cases (e.g. R = Ph), equilibria between these two forms were observed in solution. We have so far been unable to synthesize the 2,2-dppp analogue of $[MePt(\mu\text{-Cl})(\mu\text{-dppm})_2PtMe]Cl$; even heating **11** in ethanol with $NaBPh_4$ did not result in the formation of $[MePt(\mu\text{-Cl})(\mu\text{-2,2-dppp})_2PtMe]BPh_4$ or any other binuclear species ($^{31}P\{^1H\}$ NMR spectroscopic evidence).

We next attempted to carry out reactions known to form "face-to-face" dimers of the type *trans,trans*-$[Pt_2R_4(\mu\text{-dppm})_2]$ with the dppm system. For example, whereas treatment of $[PtCl_2(dppm\text{-}P,P')]$ with NaCN in ethanol gave *trans,trans*-$[Pt_2(CN)_4(\mu\text{-dppm})_2]$,[8] treatment of **7** with NaCN under the same conditions gave, exclusively, $[Pt(CN)_2(2,2\text{-dppp-}P,P')]$ (**12**). Although **12** was too insoluble for reliable ^1H NMR spectra to be obtained, and the $^{31}P\{^1H\}$ NMR spectrum was noisy, the observation of a singlet at −10.9 ppm (i.e. upfield from the free ligand), with a $^1J_{PtP}$ of 2002 Hz (appropriate for P-*trans*-CN for a four-membered chelate diphosphine, but too small to be due to P-*trans*-P), is good evidence for the mononuclear chelate structure we assign to **12**. Two bands are expected in the IR spectrum due to ν_{CN} for the chelate complex. Although only one band was observed, at 2130 cm^{-1}, this was rather broad. Interestingly, when we treated the salt **9** with 2 equiv of NaCN in methanol, the product (albeit isolated in only moderate yield) was again **12**. This contrasts with the behavior of $[Pt(dppm\text{-}P,P')_2]Cl_2$, which reacts under

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these conditions to give $[Pt(CN)_2(dppm\text{-}P)_2]$ in good yield.[8]

Treatment of $[PtCl_2(dppm)]$ with LiC≡CPh gave *trans, trans*-$[Pt_2(C{\equiv}CPh)_4(\mu\text{-}dppm)_2]$,[7] and although $[Pt(C{\equiv}CMe)_2(dppm\text{-}P,P')]$ has been prepared, from $[PtCl_2(dppm)]$ and HC≡CMe/NaOMe/MeOH, it rearranges in solution to the "face-to-face" dimer in the presence of traces of free phosphine.[12] In contrast, we find that reaction of **7** with LiC≡CPh gives only $[Pt(C{\equiv}CPh)_2(2,2\text{-}dppp\text{-}P,P')]$ (**13**), in moderate yield, and that **13** has no tendency to rearrange to a dimer in solution, in the presence of LiC≡CPh, PPh_3, or 2,2-dppp as catalyst. Again, the main evidence for the structure of **13** is that the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −15.4 ppm, with a $^1J_{PtP}$ value of 2031 Hz, too small for P-*trans*-P but in the right range for P-*trans*-C≡CR. Additionally, the infrared spectrum (Nujol mull) shows two bands assigned to $\nu_{C\equiv C}$, at 2105 and 2097 cm^{-1}. The complex $[Pt(C{\equiv}CBu^n)_2(2,2\text{-}dppp\text{-}P,P')]$ (**14**) was also prepared from **7** and LiC≡CBu^n, albeit in low yield.

We found that **13** could also be prepared in better yield by the reaction of **7** with hydrazine hydrate and excess HC≡CPh in ethanol, a reaction which has often previously been employed to make the complexes *trans*-$[Pt(C{\equiv}CPh)_2(PR_3)_2]$.[48]

It is interesting that, in a study of propynylplatinum(II) complexes of ligands $R_2PCH_2PR_2$, Puddephatt found that various isomers of dimeric, diphosphine-bridged complexes were favored in solution when R = Me, Et, or Ph but that when R = Pr^i, only the chelate form $[Pt(C{\equiv}CMe)_2(Pr^i_2PCH_2PPr^i_2)]$ could be isolated.[12] Clearly, the behavior of 2,2-dppp mimics that of the latter bulky, electron-rich diphosphine.

Although *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ compounds are readily prepared from *trans,trans*-$[Pt_2(C{\equiv}CR)_4(\mu\text{-}dppm)_2]$ and additional dppm and have been used as precursors to dppm-bridged heterobimetallic complexes,[7] **13** and **14** show no tendency to react with further 2,2-dppp to afford *trans*-$[Pt(C{\equiv}CR)_2(2,2\text{-}dppp\text{-}P)_2]$ ($^{31}P\{^1H\}$ NMR spectroscopic evidence). Moreover, whereas treatment of $[Pt(dppm\text{-}P,P')_2]Cl_2$ with LiC≡CR gave ring-opened *trans*-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (in low yield because of competing deprotonation to give $[Pt(Ph_2PCHPPh_2)_2]$[7]), we found that treatment of the salt **9** with 2 equiv of LiC≡CPh gave only **13** and free 2,2-dppp. Moreover, whereas the salts $[Pt(dppm)_2]X_2$ (X = Cl, Br, I) react with $Hg(C{\equiv}CR)_2$ to give the heterobimetallic complexes *trans*-$[Pt(C{\equiv}CR)_2(\mu\text{-}dppm)_2HgX_2]$, the reaction of **9** with $Hg(C{\equiv}CPh)_2$ again gave only a moderate yield of **13** and free 2,2-dppp.

In summary, the coordination chemistry of 2,2-dppp with Ni^{II}, Pd^{II}, and Pt^{II} is dominated by the strong tendency for the formation of four-membered chelate rings with this ligand. Reactions which, with dppm chelate complexes, result in ring opening to give $Pt(\eta^1\text{-}dppm)_2$ or $Pt(\mu\text{-}dppm)_2Pt$ species, result only in ligand metatheses with the corresponding 2,2-dppp complexes. No evidence for chelate ring-opening reactions with Pt^{II} or Pd^{II} complexes of the latter ligand has been found. Moreover, the chelate complexes **1** and **2** are much more robust than the corresponding $[NiX_2(dppm)]$ and are catalytically active in Kumada-type coupling reactions. The coordination chemistry of 2,2-dppp appears to mimic that of diphosphines bearing bulky substituents at phosphorus, such as $Pr^i_2PCH_2PPr^i_2$ or $^tBu_2PCH_2P^tBu_2$. It will be interesting in the future to investigate whether "bent 14-electron" fragments [M(2,2-dppp)] (M = Ni, Pd, Pt), or [Rh(2,2-dppp)Cl], analogous to $[M(^tBu_2PCH_2P^tBu_2)]$ and $[Rh(^tBu_2PCH_2P^tBu_2)Cl]$,[13,14,30] can be generated, and the stability of the four-membered chelate rings formed by this ligand will enable investigations of the role of this unusual ring size in homogeneous catalysis.

Experimental Section

Methods and Reagents. General methods were as described in previous papers from this laboratory,[23] except that some fast atom bombardment mass spectra were run at the EPSRC National Mass Spectrometry Service (Swansea, U.K.). All reactions were performed under a nitrogen atmosphere. Petroleum ether was of boiling range 40−60 °C. IR spectra were recorded on Nujol mulls between CsI plates. The ligand 2,2-bis(diphenylphosphino)propane (2,2-dppp) was prepared from 2,2-dichloropropane (Aldrich Chemical Co.) by the literature method,[50] except that the product was recrystallized under nitrogen from dichloromethane−ethanol. Characterizing data were as previously reported.[28] The pure, dry solid isolated in this way is air-stable, but in an impure or wet state, or in solution, the ligand is air-sensitive.

Preparation of $[NiCl_2(2,2\text{-}dppp)]$ (1). A solution of $[Ni(H_2O)_6]Cl_2$ (0.12 g, 0.5 mmol) in EtOH (10 cm^3) was treated with the ligand (0.206 g, 0.5 mmol), and the mixture was refluxed for 10 min. Solvent volume was reduced to ca. 3 cm^3, and the red-orange microcrystalline solid that precipitated was filtered off and dried in vacuo. Yield: 0.265 g, 84%. Selected data for **1** are as follows. Anal. Found: C, 60.07; H, 4.86. Calcd for $C_{27}H_{26}Cl_2NiP_2$: C, 59.87; H, 4.84. IR: ν_{Ni-Cl} 355, 326 cm^{-1}. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −8.1. ^1H NMR (200 MHz; $CDCl_3$): 1.23, t, $^3J_{PH}$ = 16.4 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 542 (M), 507 (M − Cl), 471 (M − HCl − Cl).

Preparation of $[NiBr_2(2,2\text{-}dppp)]$ (2). Preparation was as for **1**, using $[Ni(H_2O)_6]Br_2$ (0.21 g, 0.64 mmol) and 2,2-dppp (0.26 g, 0.64 mmol) in EtOH (15 cm^3). Yield: 0.24 g, 60%. Selected data for **2** are as follows. Anal. Found: C, 51.10; H, 4.10. Calcd for $C_{27}H_{26}Br_2NiP_2$: C, 51.39; H, 4.15. IR: ν_{Ni-Br} 287 cm^{-1}. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −1.5. ^1H NMR (200 MHz; $CDCl_3$): 1.28, t, $^3J_{PH}$ = 16.3 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 630 (M).

Preparation of $[Ni(2,2\text{-}dppp)_2](ClO_4)_2$ (3). A solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.43 g, 1.20 mmol) in EtOH (20 cm^3) was treated with the ligand (1.0 g, 2.43 mmol), and the mixture was brought to reflux. After 5 min, it was cooled to room temperature, and the light yellow precipitate was filtered off, washed with EtOH (2 × 5 cm^3), and dried in vacuo. Yield: 1.07 g, 83%. Selected data for **3** are as follows. Anal. Found: C, 59.69; H, 7.79. Calcd for $C_{54}H_{52}Cl_2NiO_8P_4$: C, 59.92; H, 4.84. IR: ν_{Cl-O} 1060 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −2.0. ^1H NMR (200 MHz; $CDCl_3$): 1.76, virtual quintet, apparent $^3J_{PH}$ = 8.0 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 981 (M − ClO_4), 881 (M − $HClO_4$ − ClO_4).

Preparation of $[PdCl_2(2,2\text{-}dppp)]$ (4). The ligand (0.27 g, 0.65 mmol) was added to a solution of $[PdCl_2(PhCN)_2]$ (0.25 g, 0.65 mmol) in CH_2Cl_2 (40 cm^3), and the solution was refluxed gently for 30 min and then cooled. The volume was reduced to ca. 5 cm^3, and addition of Et_2O (30 cm^3) yielded a white precipitate, which was filtered off, dried, and recrystallized from CH_2Cl_2−MeOH to afford white crystals. Yield: 0.32 g, 83%. Selected data for **4** are as follows. Anal. Found: C,

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54.91; H, 4.24. Calcd for $C_{27}H_{26}Cl_2P_2Pd$: C, 54.99; H, 4.44. IR: ν_{Pd-Cl} 315, 290 cm^{-1}. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −13.5. ^1H NMR (200 MHz; $CDCl_3$): 1.34, t, $^3J_{PH}$ = 17.4 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 554 (M − Cl), 518 (M − HCl − Cl).

Preparation of [PdI$_2$(2,2-dppp)] (5). (a) From 4. To a stirred suspension of **5** (0.20 g, 0.34 mmol) in acetone (20 cm^3) was added NaI (0.51 g, 3.4 mmol). The solution turned yellow and the suspended solid dissolved. After 1 h, the volume was reduced to ca. 5 cm^3 under reduced pressure, the solution was filtered, and Et_2O (15 cm^3) was added. The yellow precipitate was filtered at the pump, washed successively with water, ethanol, and diethyl ether, dried in vacuo, and recrystallized from CH_2Cl_2/Et_2O. Yield: 0.18 g, 69%. Orange-yellow needle crystals of **5** suitable for X-ray crystallography were grown from CH_2Cl_2/MeOH by diffusion. Selected data for **5** are as follows. Anal. Found: C, 40.00; H, 3.22. Calcd for $C_{27}H_{26}I_2P_2Pd\cdot 0.75CH_2Cl_2$: C, 39.84; H, 3.31. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −19.1. ^1H NMR (200 MHz; $CDCl_3$): 1.29, t, $^3J_{PH}$ = 16.0 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 772 (M), 645 (M − I), 517 (M − I − HI).

(b) From Pd(OAc)$_2$. To a solution of $Pd(OAc)_2$ (0.20 g, 0.89 mmol) in CH_2Cl_2 (10 cm^3) was added 2,2-dppp (0.36 g, 0.89 mmol), followed by a solution of NaI (0.39 g, 2.6 mmol) in acetone (10 cm^3). The mixture was set aside at room temperature, and orange crystals separated. These were filtered off and dried. Yield: 0.40 g, 59%. Further, less pure product was precipitated on addition of petroleum ether (10 cm^3).

Preparation of [Pd(2,2-dppp)$_2$](BF$_4$)$_2$ (6). To [$PdCl_2$-$(PhCN)_2$] (0.46 g, 1.20 mmol) in CH_2Cl_2 (25 cm^3) was added sequentially $AgBF_4$ (0.49 g, 1.2 mmol), CH_3CN (35 cm^3), and 2,2-dppp (1.04 g, 2.52 mmol). The mixture was stirred at room temperature for 1 h and then filtered through a Kieselguhr pad. Solvent was removed *in vacuo*, and the residue was taken up in CH_3CN (5 cm^3) and precipitated with Et_2O to give a pale yellow solid, which was filtered off and dried in vacuo. Yield: 1.07 g, 83%. The analytical sample was recrystallized from CH_2Cl_2/Et_2O. Selected data for **6** are as follows. Anal. Found: C, 56.89; H, 4.69. Calcd for $C_{54}H_{52}B_2F_8P_4Pd\cdot 0.5CH_2$-$Cl_2$: C, 57.06; H, 4.65. IR: ν_{B-F} 1058 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −2.1. ^1H NMR (200 MHz; $CDCl_3$): 1.77, virtual quintet, apparent $^3J_{PH}$ = 8.8 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 1017 (M − BF_4), 930 (M − HBF_4 − BF_4).

Preparation of [PtCl$_2$(2,2-dppp)] (7). To a solution of [$PtCl_2(PhCN)_2$] (0.472 g, 1.00 mmol) in CH_2Cl_2 (35 cm^3) was added the ligand (0.412 g, 1.00 mmol). The mixture was refluxed for 10 min. White crystals separated. The solvent volume was reduced to ca. 10 cm^3, and the product was then filtered off and dried in vacuo. Yield: 0.46 g, 68%. Further product could be obtained by the addition of Et_2O to the mother liquor. Selected data for **7** are as follows. Anal. Found: C, 45.78; H, 3.67. Calcd for $C_{27}H_{26}Cl_2P_2Pt\cdot 0.5CH_2Cl_2$: C, 45.82; H, 3.77. IR: ν_{Pt-Cl} 310, 290 cm^{-1}. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −24.2, $^1J_{Pt-P}$ 3135 Hz. ^1H NMR (200 MHz; $CDCl_3$): 1.22, t, $^3J_{PH}$ = 17.2 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 678 (M), 643 (M − Cl).

Preparation of [PtI$_2$(2,2-dppp)] (8). To **7** (0.25 g, 0.37 mmol), partially dissolved in acetone (30 cm^3), was added NaI (0.55 g, 3.7 mmol). After 1 h of stirring at room temperature, the volume was reduced to 5 cm^3 at the pump, and Et_2O (10 cm^3) was added. The resulting yellow precipitate was filtered off, washed successively with water, ethanol, and diethyl ether, and dried in vacuo. Yield: 0.22 g, 68%. Selected data for **8** are as follows. Anal. Found: C, 37.55; H, 3.06. Calcd for $C_{27}H_{26}I_2P_2Pt$: C, 37.66; H, 3.04. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −27.9, $^1J_{Pt-P}$ 2928 Hz. ^1H NMR (200 MHz; $CDCl_3$): 1.18, t, $^3J_{PH}$ = 16.8 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 861 (M), 734 (M − I).

Preparation of [Pt(2,2-dppp)$_2$]Cl$_2$ (9). A solution of [$PtCl_2(PhCN)_2$] (0.20 g, 0.5 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise to a solution of the ligand (0.42 g, 1.0 mmol) in EtOH (15 cm^3) under reflux. After 2 h, the mixture was cooled, and the solvent was removed in vacuo. The residue was recrystallized from MeOH/Et_2O. Yield: 0.35 g, 64%. Selected data for **9** are as follows. Anal. Found: C, 59.40; H, 4.70. Calcd for $C_{54}H_{52}Cl_2P_4Pt$: C, 59.46; H, 4.81. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −21.6, $^1J_{Pt-P}$ 2268 Hz. ^1H NMR (200 MHz; $CDCl_3$): 1.80, virtual quintet, apparent $^3J_{PH}$ = 8.4 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 1055 (M − Cl), 1020 (M − HCl − Cl).

Preparation of [PtMe$_2$(2,2-dppp)] (10). (a) From 7. A finely ground sample of **7** (0.25 g, 0.369 mmol) suspended in dry thf (2 cm^3) was treated with a solution of MeLi (1.5 cm^3 of a 1.45 M solution in Et_2O; 2.18 mmol) dropwise at 0 °C with stirring. The mixture was warmed to room temperature and after 16 h was brought to reflux for 15 min and then cooled to 0 °C. The clear solution was worked up by the addition of MeOH (3 drops), and the solvent was removed in vacuo. The residue was recrystallized from CH_2Cl_2 and MeOH as white microcrystals. Yield: 0.105 g, 45%. Selected data for **10** are as follows. Anal. Found: C, 54.57; H, 5.01. Calcd for $C_{29}H_{32}P_2Pt$: C, 54.65; H, 5.06. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −2.8, $^1J_{Pt-P}$ 1577 Hz. ^1H NMR (200 MHz; $CDCl_3$): 1.29, t, $^3J_{PH}$ = 14.4 Hz ($PC(CH_3)_2P$); 0.83, t, $^3J_{PH}$ = 6.7 Hz, $^2J_{PtH}$ = 72.7 Hz ($Pt(CH_3)_2$). MS (FAB): *m/e* 622 (M − Me), 606 (M − Me − CH_4).

(b) From [PtMe$_2$(COD)]. The ligand (0.260 g, 0.63 mmol) was added to a solution of [$PtMe_2$(COD)] (0.205 g, 0.62 mmol) in CH_2Cl_2 (5 cm^3). The mixture was refluxed for 15 min and evaporated to dryness, and the residue was then triturated with MeOH. The white product was filtered off and dried in vacuo. Yield: 0.365 g, 92%.

Preparation of [PtCl(Me)(2,2-dppp)] (11). A solution of HCl in MeOH (1.0 cm^3) was generated from the methanolysis of acetyl chloride (26 μL, 0.37 mmol) and was added to a solution of **10** (0.237 g, 0.372 mmol) in CH_2Cl_2 (3 cm^3). Gas was evolved, and after 10 min, colorless crystals appeared. The mixture was set aside for 16 h at 4 °C, and the product was then filtered off and dried in vacuo. Yield: 0.17 g, 76%. Selected data for **11** are as follows. Anal. Found: C, 51.20; H, 4.41; Cl, 5.6. Calcd for $C_{28}H_{29}ClP_2Pt$: C, 51.11; H, 4.44; Cl, 5.39. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −0.7, d, $^1J_{Pt-P}$ 1342 Hz, $^2J_{PP}$ 24 Hz (P−*trans*-CH_3); −2.9, d, $^1J_{Pt-P}$ 3965 Hz, $^2J_{PP}$ 24 Hz (P−*trans*-Cl). ^1H NMR (200 MHz; $CDCl_3$): 1.30, 6H, t, $^3J_{PH}$ = 14.7 Hz ($PC(CH_3)_2P$); 0.87, 3H, dd, $^3J_{PH}$ = 8.1 Hz (trans), 2.5 Hz (cis), $^2J_{PtH}$ = 59.5 Hz ($PtCH_3$).

Preparation of [Pt(CN)$_2$(2,2-dppp)] (12). A suspension of **7** (0.20 g, 0.29 mmol) in EtOH (25 cm^3) was refluxed with NaCN (0.029 g, 0.59 mmol) for 16 h. The colorless product was filtered off, washed with successively water (10 cm^3), ethanol (10 cm^3), and CH_2Cl_2 (2 cm^3), and dried in vacuo. Yield: 0.18 g, 88%. Selected data for **12** are as follows. Anal. Found: C, 51.59; H, 3.71; N, 3.90. Calcd for $C_{29}H_{26}N_2P_2Pt\cdot 0.25CH_2Cl_2$: C, 51.60; H, 3.92; N, 4.11. IR: ν_{CN} 2130 cm^{-1} (m, broad). $^{31}P\{^1H\}$ NMR (101.2 MHz; CH_2Cl_2/CD_2Cl_2): δ −10.9, $^1J_{Pt-P}$ 2002 Hz.

Preparation of [Pt(C≡CPh)$_2$(2,2-dppp)] (13). (a) From 7 and LiC≡CPh. To a suspension of finely ground **7** (0.20 g, 0.29 mmol) in thf (0.5 cm^3) was added a solution of LiC≡CPh (0.79 mmol) in thf (3 cm^3) at 0 °C. The mixture was stirred for 4 h and then warmed to reflux for 10 min, cooled, and evaporated to dryness under reduced pressure. The residue was triturated with MeOH and filtered. The crude product (0.12 g) was recrystallized from CH_2Cl_2/MeOH. Yield: 0.09 g, 42%. Selected data for **13** are as follows. Anal. Found: C, 63.70; H, 4.51. Calcd for $C_{43}H_{36}P_2Pt$: C, 63.79; H, 4.48. IR: $\nu_{C\equiv C}$ 2105, 2097 cm^{-1}. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −15.5, $^1J_{Pt-P}$ 2035 Hz. ^1H NMR (200 MHz; $CDCl_3$): 1.44, t, $^3J_{PH}$ = 15.4 Hz ($PC(CH_3)_2P$). MS (FAB): *m/e* 810 (M), 708 (M − C≡CPh), 606 (M − HC≡CPh − C≡CPh).

(b) From 7 and HC≡CPh/Hydrazine. To a suspension of finely ground **7** (0.20 g, 0.29 mmol) in ethanol (1.5 cm^3) was

added $H_2NNH_2 \cdot H_2O$ (0.106 g, 2.10 mmol). The solution was brought to reflux for 2 min, after which HC≡CPh (0.21 g, 2.10 mmol) was added. Refluxing was continued for 10 min, during which time a clear orange solution formed. This was set aside for 16 h at 0 °C. The light yellow plates which crystallized were filtered off and dried in vacuo. Yield: 0.13 g, 61%.

Preparation of [Pt(C≡CBu^n)$_2$(2,2-dppp)] (14). A solution of LiC≡CBu^n (1.11 mmol) in thf (2 cm^3) and hexane (0.7 cm^3) was treated with finely ground **8** (0.25 g, 0.369 mmol) at −78 °C. The solution was stirred, allowed to reach room temperature, and set aside for 3 h. It was then briefly refluxed, cooled, and evaporated to ca. 2 cm^3 volume. On addition of Et_2O, a light brown precipitate was obtained. This was filtered off and dried in vacuo. Yield: 0.043 g, 15%. Selected data for **14** are as follows. Anal. Found: C, 60.59; H, 5.73. Calcd for $C_{39}H_{44}P_2Pt$: C, 60.82; H, 5.76. $^{31}P\{^1H\}$ NMR (101.2 MHz; $CDCl_3$): δ −16.6, $^1J_{Pt-P}$ 2024 Hz. ^1H NMR (200 MHz; $CDCl_3$): 2.42, t, $^3J_{HH}$ 7.0 Hz ($C{\equiv}CCH_2R$), 1.37, t, $^3J_{PH}$ = 15.4 Hz ($PC(CH_3)_2P$), 1.33, m ($CH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$), 0.72, t, $^3J_{HH}$ 7.0 Hz ($CH_2C\mathbf{H}_3$). MS (FAB): *m*/*e* 770 (M), 688 (M − C≡CBu^n), 606 (M − HC≡CBu^n − C≡CBu^n).

X-ray Crystal Structure Determination of [PdI$_2$(2,2-dppp-*P*,*P*′)]·0.8CH$_2$Cl$_2$ (5·0.8CH$_2$Cl$_2$). The crystal structure was solved by direct methods.[51,52] Three representative reflections, remeasured after every 150 reflections, remained unchanged throughout data collection. An empirical absorption correction, using the program DIFABS,[53] was applied, which resulted in transmission factors ranging from 0.75 to 1.16. The data were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in idealized positions (d_{C-H} = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the B_{equiv} value of the atom to which they were bonded. Details of the data collection, structure solution, and refinement are summarized in Table 2.

Acknowledgment. Thanks are expressed to the EPSRC for a studentship (M.K.M.), for an allocation at the National Mass Spectrometry Service, Swansea, U.K., and for access to the Chemical Database Service, Daresbury, U.K., and to Johnson-Matthey for a generous loan of platinum metal salts.

Supporting Information Available: Tables giving positional and thermal parameters, bond distances and angles, and torsion or conformational angles for **5**·0.8CH_2Cl_2 (14 pages). Ordering information is given on any current masthead page.

OM970941T

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