excess (ca. 2 mL) of aqueous 6 M NaOH was added while vigorously stirring. The CH_2Cl_2 layer became yellow-orange. Solvent was removed by pumping at room temperature. The residue was dissolved in THF (it is insoluble in hexane) and filtered through Celite to give an orange solution, having ν(CO) at 1910 (vs) cm^{-1} and ν(NN) at 1615 (s) cm^{-1}. The THF was pumped off and the oily residue was now easily extracted into hexane to give an orange solution having ν(CO) 1925 (vs) and ν(NN) 1619 (s) cm^{-1}. The hexane solution was chromatographed on neutral alumina. Elution with benzene gave a yellow solution. Benzene was pumped off, and the yellow residue was dissolved in pentane from which **8** precipitated as a yellow solid during 6 h at −78 °C in 80% yield: decomposes at 95–98 °C; IR (hexane) 1925 (vs, ν(CO)), 1619 (s) cm^{-1} (ν(NN)), (CH_2Cl_2) 1906 (vs), 1618 (s) cm^{-1}; ^1H NMR (C_6D_6) δ −5.88 (s, 1 H, ReH), 1.90 (s, 15 H, C_5Me_5), 3.27 (s, 3 H, OMe), 6.78 (d, 2 H), 7.61 (d, 2 H, C_6H_4); MS (16 eV), m/e 484, 486 (M^+) 456, 458 ($M - CO^+$). Anal. Calcd for **9**: C, 44.53; H, 4.74; N, 5.77. Found: C, 45.44; H, 5.23; N, 5.71.

Preparation of Li[(η-C_5Me_5)Re(CO)(p-$N_2C_6H_4OMe$)(CO_2)]. Method 1. The hydroxycarbonyl **8** (100 mg) was suspended in hexane (25 mL) and excess (0.5 mL) of MeLi (1.6 M in diethyl ether) was added under N_2 with vigorous stirring. After 30 min the solvent was removed by pipet and the yellow solid washed twice with 5 mL of hexane. It was redissolved in CH_2Cl_2, filtered under N_2, and reprecipitated by adding hexane as a yellow solid in near quantitative yield: CH_2Cl_2 was observed to be present by MS; IR (CH_2Cl_2, cm^{-1}) 1928 (vs, ν(CO)), 1614 (s, ν(NN)), (THF) 1907 (vs), 1612 (s); ^1H NMR (D_2O) δ 2.03 (15 H, C_5Me_5), 3.81 (s, 3 H, OMe), 7.02 (d, 2 H), 7.28 (d, 2 H, C_6H_4). Anal. Calcd for Li[(η-C_5Me_5)Re(CO)(p-$N_2C_6H_4OMe$)(CO_2)]·CH_2Cl_2: C, 38.77; H, 3.88; N, 4.52. Found: C, 38.32; H, 4.18; N, 4.76.

Method 2. The dicarbonyl [(η-C_5Me_5)Re(CO)$_2$(p-$N_2C_6H_4OMe$)][BF_4] (**7**) was dissolved in CH_2Cl_2 and stirred with an excess of saturated aqueous LiOH. Within a few minutes the CH_2Cl_2 layer became orange-yellow. This was separated from the colorless aqueous layer by pipet and solvent removed to give the product as a yellow solid (soluble in water and insoluble in hexane) in quantitative yield.

Treatment of **7** with excess NaOD in D_2O produced a yellow solution of the carboxylate anion with ^1H NMR parameters δ 2.00 (15 H, C_5Me_5), 3.79 (3 H, OMe), 7.00 (d, 2 H), 7.26 (d, 2 H, C_6H_4) virtually identical with those of the lithium salt.

Preparation of (η-C_5Me_5)Re(CO)(p-$N_2C_6H_4OMe$)(OCHO) (11). Compound **12** (70 mg) in acetone (25 mL) was stirred with finely ground solid sodium formate, then water (10 mL) was added, and the reaction was followed by IR. All of **12** had reacted in 1 h. Solvent was pumped off, and the residual water was pipetted from the red-orange product which was then dissolved in ether and filtered through Celite. Addition of hexane precipitated a red-orange solid: mp 65–67 °C; 85% yield; IR (acetone) 1931 (vs, ν(CO)), 1645 (m), 1620 (s) cm^{-1}, (ether) 1941 (vs), 1648 (m), 1622 (s) cm^{-1}, (CH_2Cl_2) 1925 (vs), 1642 (m), 1624 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (s, 15 H, C_5Me_5), 3.81 (s, 3 H, OMe), 6.92 (d, 2 H), 7.29 (d, 2 H, C_6H_4), 8.03 (s, 1 H, OCHO), (C_6D_6) δ 1.73 (s), 3.22 (s), 6.74 (d), 7.63 (d), 8.37 (s); MS (EI, 15 eV, 75 °C, based on ^{187}Re), m/e 530 (M^+), 502 ($M - CO^+$), 486 ($M - CO_2^+$) in 1:5:3 ratio; MS (FAB, xenon, sulfolane, based on ^{187}Re), m/e 513 ($M - OH^+$), 502 ($M - CO^+$), 485 ($M - HCO_2^+$), 429 ($M - N_2 - CO - HCO_2^+$). Anal. Calcd for **11**: C, 43.10; H, 4.34; N, 5.29. Found: C, 43.53; H, 4.40; N, 5.34.

Preparation of [(η-C_5Me_5)Re(CO)(CH_3CN)(p-$N_2C_6H_4OMe$)][BF_1] (12). An approximate 20% stoichiometric excess of iodosobenzene was added as a solid to a stirred solution of **7** (50 mg) in CH_3CN (15 mL). After 30 min, all of **7** had reacted (by IR) and no further change occurred. Removal of solvent under vacuum gave a red oily solid which was recrystallized from acetone–ether as an orange microcrystalline solid: mp 65–67 °C; 91% yield; IR (acetone) 1958 (vs, ν(CO)), 1655 (s, ν(NN)), (CH_3CN) 1959 (vs), 1658 (s), (CH_2Cl_2) 1962 (vs), 1658 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.14 (s, 15 H, C_5Me_5), 3.10 (s, 3 H, CH_3CN), 3.85 (s, 3 H, OMe), 7.05 (d, 2 H), 7.24 (d, 2 H, C_6H_4); MS (FAB), sulfolane, xenon, based on ^{187}Re), m/e 526 (M^+ of cation), 485 ($M^+ - MeCN$). Anal. Calcd for **12**: C, 39.21; H, 4.08; N, 6.86. Found: C, 38.77; H, 4.18; N, 6.63.

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Registry No. **1a**, 81028-25-3; **1b**, 81028-27-5; **1c**, 81028-31-1; **2a**, 86688-81-5; **2b**, 86688-82-6; **2c**, 86688-83-7; **3a**, 86688-84-8; **3b**, 86688-85-9; **3c**, 86688-86-0; **4b**, 94405-77-3; **4b**·Li, 94405-76-2; **4b**·Ca, 94405-78-4; **5**, 94405-79-5; **6**, 94405-81-9; **7**, 92786-90-8; **8**, 94405-82-0; **9**, 94405-83-1; **10b**, 94405-85-3; **10b**·Li, 94405-84-2; **11**, 94405-86-4; **12**, 94405-88-6; (η-C_5H_5)Re(CO)$_2$(Na), 36543-62-1; (η-C_5Me_5)Re(CO)$_3$, 12130-88-0; [p-$N_2C_6H_4OMe$][BF_4], 459-64-3; iodosobenzene, 536-80-1.

New Structural Forms of Alkynylplatinum(II) Complexes with $R_2PCH_2PR_2$ Ligands

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The complexes [$PtCl_2$(L-L)] react with MeC≡CH and NaOR in ROH to give the monomeric, bis(acetylide) compounds [Pt(C≡CMe)$_2$(L-L)]. (L-L = depm and dippm, R = Et; L-L = dppm, R = Me). [Pt_2Cl_4(dmpm)$_2$] reacts with MeC≡CH and NaOMe in MeOH to give the dimeric acetylide complex *cis,cis*-[Pt_2(C≡CMe)$_4$(dmpm)$_2$]. The complex [Pt(C≡CMe)$_2$(dppm)] rearranges in solution to give *trans,trans*-[Pt_2(C≡CMe)$_4$(dppm)$_2$], catalyzed by a trace amount of dppm, while [Pt(C≡CMe)$_2$(depm)] rearranges to a mixture of all three possible isomers of [Pt_2(C≡CMe)$_4$(depm)$_2$] (i.e., cis,cis, cis,trans, and trans,trans), catalyzed by PPh_3. Addition of PPh_3 to [Pt(C≡CMe)$_2$(dippm)] leads only to decomposition. All products are characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy and, in some cases, by elemental analysis.

Introduction

There has recently been interest in [bis(diphenylphosphino)methane]platinum acetylide complexes.[1-3] Reaction of [$PtCl_2$(dppm)] with LiC≡CR produced the "face-to-face" diplatinum complexes of the type *trans*,-

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Table I. $^{31}P\{^1H\}$ NMR Spectra of Compounds in CD_2Cl_2 at 25 °C

compd	$\delta(^{31}P)$	$^1J(PtP)$, Hz	$^3J(PtP)$, Hz	$^2J(PP)$, Hz	$^4J(PP)$, Hz	N^1,[b] Hz
$[Pt(C{\equiv}CMe)_2(dppm)]$	−58.96	1928				
$[Pt(C{\equiv}CMe)_2(depm)]$	−52.06	1886				
$[Pt(C{\equiv}CMe)_2(dippm)]$	−33.50	1917				
cis,cis-$[Pt_2(C{\equiv}CMe)_4(dmpm)_2]$	−21.81	2216	+77	26.0	11.5	2294
trans,trans-$[Pt_2(C{\equiv}CMe)_4(dppm)_2$	−0.82	2866	+50	28.3	0	2916
cis,cis-$[Pt_2(C{\equiv}CMe)_4(depm)_2]$	−0.44	2265	+77	27.9	11.9	2342
cis,trans-$[Pt_2(C{\equiv}CMe)_4(depm)_2]$	−1.39	2342	102	17.1	17.1	unres[a]
	−0.32	2497	unres[a]	17.1	17.1	unres[a]
trans,trans-$[Pt_2(C{\equiv}CMe)_4(depm)_2]$	+3.16	2358	+26	15.7	0	2384

[a] unres = unresolved. [b] $N^1 = {}^1J(PtP) + {}^3J(PtP)$.

Table II. ^1H NMR Spectra in CD_2Cl_2 at 25 °C

	PCH_2P			$C{\equiv}CCH_3$	
compd	$\delta(CH_2)$	$^2J(PtH)$, Hz	$^3J(PtH)$, Hz	$\delta(CH_3)$	$^4J(PtH)$, Hz
$[Pt(C{\equiv}CMe)_2(dppm)]$	+4.48	10.2	32.0	+2.05	16.6
$[Pt(C{\equiv}CMe)_2(depm)]$	+3.08	9.6	31.2	+1.93	16.0
$[Pt(C{\equiv}CMe)_2(dippm)]$[a]	+2.90	9.0	27.0	+1.83	16.2
cis,cis-$[Pt_2(C{\equiv}CMe)_4(dmpm)_2]$	+2.51	unres[b]	45.0[c]	+1.89	15.8
trans,trans-$[Pt_2(C{\equiv}CMe)_4(dppm)_2]$	+4.54	unres[b]	35.4	+1.44	14.8
trans,trans-$[Pt_2(C{\equiv}CMe)_4(depm)_2]$	+2.75	4.5	30.0	unres[b]	unres[b]

[a] $\delta(PCH(CH_3)_2) + 2.19$ (s, $^3J(HH) = 7.2$ Hz). [b] unres = unresolved. [c] Approximate value; satellites are broad.

trans-$[Pt_2(C{\equiv}CR)_4(dppm)_2]$ (R = CF_3,[2] R = C_6H_4Me-*p*, Ph, CH_2CH_2Ph, or $C(Me){=}CH_2$[3]). It was reasoned that this type of complex was stable because acetylides have a distinct preference to be mutually trans in complexes of type $[M(C{\equiv}CR)_2L_2]$ (M = Pd or Pt; R = alkyl or aryl; L = tertiary phosphine).[4] Although complexes with *cis*-acetylides are known (e.g., *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$, R = alkyl or aryl; L = tertiary phosphine),[5] prior to this work no complexes of this type had been detected with $R_2PCH_2PR_2$ ligands.

In complexes of the type $[\{PtX_2(R_2PCH_2PR_2\}_n]$ (R = Me, Et, *i*-Pr, or Ph; *n* = 1 or 2) it was found that the chelated form $[PtX_2(R_2PCH_2PR_2)]$ was favored when X = Cl and R = Et, *i*-Pr, and Ph[6] and when X = Me and R = *i*-Pr and Ph.[7,8] The cis,cis dimer $[Pt_2X_4(R_2PCH_2PR_2)_2]$ was favored for X = Cl and R = Me and for X = Me and R = Me and Et. The nuclearity of such complexes was proposed to be primarily due to the steric effects of the R groups on the phosphine ligand,[6] with bulky R groups favoring monomeric structures.

Results and Discussion

The reaction of $[PtCl_2(depm)]$ or $[PtCl_2(dippm)]$ with MeC≡CH and NaOEt in EtOH and the reaction of $[PtCl_2(dppm)]$ with MeC≡CH and NaOMe in MeOH gave monomeric $[Pt(C{\equiv}CMe)_2(depm)]$, $[Pt(C{\equiv}CMe)_2(dippm)]$, and $[Pt(C{\equiv}CMe)_2(dppm)]$ of structure 1 (depm = $Et_2PCH_2PEt_2$, dippm = *i*-Pr_2PCH_2P-*i*-Pr_2, and dppm = $Ph_2PCH_2PPh_2$). The complexes were characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy (Tables I and II, respectively) and elemental analysis (Experimental Section). The $^{31}P\{^1H\}$ NMR spectra contained only a singlet, with singlet satellites of one-fourth intensity due to coupling to ^{195}Pt and with a high-field shift compared to the free phosphine ligands, as expected for chelate complexes.[9] For $[Pt(C{\equiv}CMe)_2(R_2PCH_2PR_2)]$ the magnitudes of the coordination shift, defined as δ (coordinated phosphine) − δ (free phosphine), were −22.2, −26.8, and −36.3 ppm for R = Et, *i*-Pr, and Ph, respectively, which were similar to those observed in $[PtCl_2(R_2PCH_2PR_2)]$.[6] The magnitude of $^1J(PtP)$, ca. 1880–1930 Hz, is typical for phosphorus trans to acetylide (e.g., in $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$, C≡CPh trans to $PMePh_2$, $^1J(PtP) = 1964$ Hz[5]). The ^1H NMR spectrum contains a triplet for the CH_2P_2 protons, due to coupling to two equivalent ^{31}P atoms, with platinum satellites, which is also indicative of a monomer.

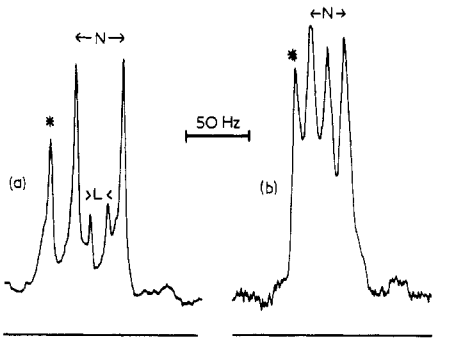

Figure 1. Low-field ^{195}Pt satellites from the ^{31}P NMR spectra (121.5 MHz) of (a) *cis,cis*-$[Pt_2(CCMe)_4(\mu\text{-dmpm})_2]$ and (b) *trans,trans*-$[Pt_2(CCMe)_4(\mu\text{-dppm})_2]$. In each case the splittings $N = {}^2J(P^AP^{A\prime}) + {}^4J(P^AP^{A\prime\prime\prime})$ and $L = {}^2J(P^AP^{A\prime}) - {}^4J(P^AP^{A\prime\prime\prime})$, and the peaks labeled asterisk are due to the $^{195}Pt_2$ isotopomer.

The reaction of $[Pt_2Cl_4(dmpm)_2]$, which is postulated to have a cis,cis structure with bridging dmpm ligands,[6] with MeC≡CH and NaOMe in MeOH produced the dimeric acetylide complex *cis,cis*-$[Pt_2(C{\equiv}CMe)_4(dmpm)_2]$, with structure 2 (dmpm = $Me_2PCH_2PMe_2$). This was characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy and by elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum contained a singlet at low field with a coordination shift of +34.7 ppm, with multiplet satellites due to both $^1J(PtP)$ and $^3J(PtP)$ couplings. The appearance of these satellites

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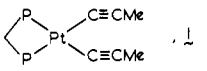
is characteristic of a cis,cis stereochemistry[8] (Figure 1).

The addition of a trace amount of dppm to a CD_2Cl_2 solution of [Pt(C≡CMe)$_2$(dppm)] promoted a slow conversion of the monomer to the "face-to-face" dimer *trans,trans*-[Pt$_2$(C≡CMe)$_4$(dppm)$_2$] with structure **4**. The



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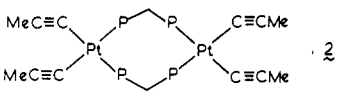

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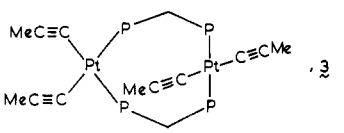

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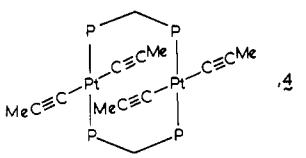

4

reaction was slow and had not reached completion after 1 month. The product was characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. No rearrangement occurred in the absence of added dppm. *trans,trans*-[Pt$_2$(C≡CMe)$_4$(dppm)$_2$] has previously been prepared by Shaw et al.[3] and our $^{31}P\{^1H\}$ NMR spectrum is identical with theirs, but we assign the outermost lines of the platinum satellites as the peaks separated by ^1J(PtP) + ^3J(PtP) (Figure 1) and not the inner lines as did Shaw. This dimer gave a coordination shift of +23.5 ppm and the trans,trans stereochemistry is shown by the "triplet" appearance of the ^{195}Pt satellites.

The addition of a trace amount of PPh_3 to a CD_2Cl_2 solution of [Pt(C≡CMe)$_2$(depm)] promoted a slow conversion of the monomer to a mixture of dimeric platinum acetylide complexes. Initially, two dimers were observed in the $^{31}P\{^1H\}$ NMR spectrum. The first of these gave a singlet, with a coordination shift of +30.3 ppm, whose platinum satellites were typical for a dimer with cis,cis geometry. The magnitudes of ^1J(PtP) and ^3J(PtP) were similar to those of the dmpm complex, so this dimer is identified as *cis,cis*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$], with structure **2**. The other dimer originally observed gave an AA^{1}BB^{1}X pattern in the $^{31}P\{^1H\}$ NMR spectrum. The platinum satellites of both P_A and P_B were triplets, showing that $J_{AB} = J_{AB}^1$ (Figure 2). This dimer is identified as *cis,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$], with structure **3**, on the basis of its $^{31}P\{^1H\}$ NMR spectrum. After several days a third dimer was also present in solution, with a singlet in the $^{31}P\{^1H\}$ NMR spectrum with a coordination shift of +33.1 ppm, and platinum satellites indicating a trans,trans stereochemistry, similar to those of *trans,trans*-[Pt$_2$(C≡CMe)$_4$(dppm)$_2$]. This dimer is therefore identified as *trans,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$], with structure **4**. Thus, with depm, all three possible stereochemistries of [Pt$_2$(C≡CMe)$_4$(depm)$_2$] are observed.

The dimer *trans,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$] was also observed in the reaction between [Pt$_2$Cl$_2$(depm)$_2$] and 2 equiv of Hg(C≡CMe)$_2$ as the major product in solution. However, attempts to isolate this dimer from larger scale reactions led to extensive decomposition, and it could not be obtained in a pure state. Reactions between [PtCl$_2$(depm)] and Hg(C≡CMe)$_2$ were extremely slow and led to much decomposition.

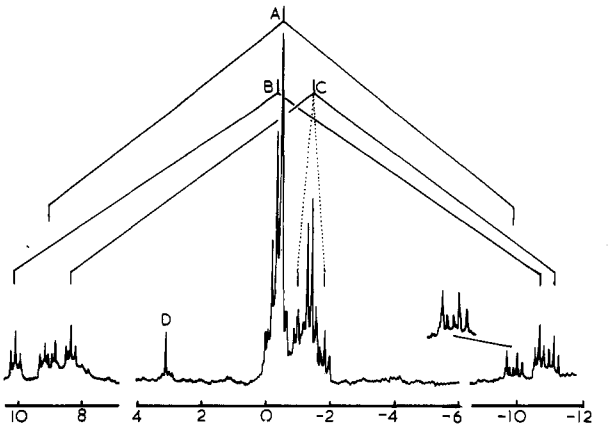

Figure 2. ^{31}P NMR spectrum (121.5 MHz) of a mixture obtained from dimerization of [Pt(CCMe)$_2$(depm)]. Peak A is due to the cis,cis isomer, peaks B and C are due to the cis,trans isomer, and peak D is due to the trans,trans isomer of [Pt$_2$(CCMe)$_4$(μ-depm)$_2$]. The centers of the ^{195}Pt satellites are indicated above.

There was no reaction when a trace of PPh_3 was added to *cis,cis*-[Pt$_2$(C≡CMe)$_4$(dmpm)$_2$], even after 10 days, and thus the cis,cis stereochemistry is probably the most stable for this dimer. Addition of PPh_3 to [Pt(C≡CMe)$_2$(dippm)] in CD_2Cl_2 or $CDCl_3$ led to decomposition. No dimeric acetylide complexes were detected, and the reaction ultimately led to formation of [PtCl$_2$(dippm)].

Conclusions

Steric hindrance in these complexes probably (as deduced from molecular models) follows the sequence cis,cis dimer **2** ≈ cis,trans dimer **3** > trans,trans dimer **4** > monomer **1**. For the bulkiest substituents, R = *i*-Pr, only the monomer **1** could be detected, and for the less bulky substituents, R = Ph, the monomer was formed but is clearly less stable than the trans,trans dimer. For the smallest substituents, R = Me, only the cis,cis dimer was formed. Only for R = Et have all the structures **1**–**4** been identified. It is apparent that these results are best interpreted in terms of steric effects of the substituents, R, being dominant in determining the preferred nuclearity and dimer stereochemistry. Only structure **4** was known previously.[1-3]

The formation of the thermodynamically less stable monomeric form **1** when R = Et or Ph in this work is clearly due to the mild conditions used. The rearrangement to the more stable dimers clearly involves reversible nucleophilic substitution at platinum by strong ligands (dppm or PPh_3 in this work, LiC≡CMe in earlier work[1-3]) with cleavage of a PtP bond to give an η^1-dppm ligand, followed by dimerization. The formation of the isomers **2** and **3** before **4**, when R = Et, strongly suggests that these substitutions occur primarily with retention of stereochemistry at platinum. Further slow isomerization of **2** and **3** to **4**, R = Et, then occurs.

This work illustrates clearly how changing the bulk of the substituents, R, in the ligands R$_2$PCH$_2$PR$_2$ can have dramatic effects on the coordination geometry and organometallic chemistry.

Experimental Section

NMR spectra were recorded with Varian XL100 (^1H), XL200 (^1H and ^{31}P), and XL300 (^{31}P) spectrometers in CD_2Cl_2 unless otherwise stated. Chemical shifts are quoted with respect to Me_4Si (^1H) or trimethylphosphate (^{31}P). Analyses were performed by Guelph Chemical Laboratories Ltd. The complexes [PtCl$_2$(depm)], [PtCl$_2$(dippm)], [PtCl$_2$(dppm)], and [Pt$_2$Cl$_4$(dmpm)$_2$]

were prepared by literature methods.[6]

[Pt(C≡CMe)$_2$(depm)]. MeC≡CH gas was bubbled through a suspension of [PtCl$_2$(depm)] (194 mg, 0.423 mmol) in EtOH (50 mL). A solution of NaOEt (prepared from 0.847 mmol of Na in 17 mL of EtOH) was added and the platinum complex rapidly dissolved, forming a yellow solution within 30 min. The EtOH was removed in vacuo, and the resulting oil was extracted with CH_2Cl_2 (30 mL) and filtered to remove NaCl. The CH_2Cl_2 was removed, the oil was dissolved in hot benzene, and addition of pentane yielded platelike crystals, yield 97 mg (49%). Anal. Calcd for [Pt(C≡CMe)$_2$(depm)]: C, 38.71; H, 6.06. Found: C, 38.45; H, 5.91.

[Pt(C≡CMe)$_2$(dippm)]. MeC≡CH gas was bubbled through a suspension of [PtCl$_2$(dippm)] (194 mg, 0.377 mmol) in EtOH (50 mL). A solution of NaOEt (prepared from 0.754 mmol of Na in 15 mL of EtOH) was added, and the platinum complex rapidly dissolved to form a pale yellow solution. The EtOH was removed, and the resultant oil was extracted with CH_2Cl_2 (30 mL) and filtered. A pale orange solid was obtained with difficulty by freeze drying from benzene, whose ^{31}P and ^1H NMR spectra showed it to be slightly impure [Pt(C≡CMe)$_2$(dippm)]; yield 150 mg (76%).

[Pt(C≡CMe)$_2$(dppm)]. MeC≡CH gas was bubbled through a suspension of [PtCl$_2$(dppm)] (200 mg, 0.308 mmol) in MeOH (50 mL). A solution of NaOMe (prepared from 0.616 mmol of Na in 15.5 mL of MeOH) was added slowly, over a period of 1 h. The mixture was stirred for a further 2 h, by which time all of the platinum complex had dissolved to form an orange solution. The MeOH was removed in vacuo, the resulting oil was dissolved in benzene, and the solution was filtered to remove NaCl. Addition of pentane gave orange crystals, yield 53 mg (26%). A further 105 mg (52%) of product was obtained by freeze drying the benzene solution. Anal. Calcd for [Pt(C≡CMe)$_2$(dppm)]: C, 56.62; H, 4.29. Found: C, 56.62; H, 4.32.

[Pt$_2$(C≡CMe)$_4$(dmpm)$_2$]. MeC≡CH gas was bubbled through a suspension of [Pt$_2$Cl$_4$(dmpm)$_2$] (160 mg, 0.199 mmol) in MeOH (80 mL) until the solution was saturated. A solution of NaOMe (from 0.796 mmol of Na in 20 mL of MeOH) was added, and the mixture was stirred under an atmosphere of MeC≡CH for 24 h, until a pale yellow solution was formed. The MeOH was removed in vacuo, and the resulting oil was extracted with benzene, giving a very insoluble, white solid, yield 112 mg, and a yellow solution. Addition of pentane to the solution precipitated a pale tan solid, yield 48 mg, (29%). Anal. Calcd for [Pt$_2$(C≡CMe)$_4$(dmpm)$_2$]: C, 32.28; H, 4.93. Found: C, 32.02; H, 5.05.

The white solid was only slightly soluble in CD_3OD, but its $^{31}P\{^1H\}$ and ^1H NMR spectra showed it also to be [Pt$_2$(C≡CMe)$_4$(dmpm)$_2$], with the cis,cis stereochemistry.

[Pt(C≡CMe)$_2$(dppm)] with dppm. [Pt(C≡CMe)$_2$(dppm)] (8.0 mg, 0.012 mmol) was dissolved in CD_2Cl_2 (0.4 mL), dppm (0.3 mg, 0.0008 mmol) was added, and the solution was observed periodically by ^{31}P and ^1H NMR spectroscopy. After 5 days signals for *trans,trans*-[Pt$_2$(C≡CMe)$_4$(dppm)$_2$] were appreciable (ca. 35% of the total ^{31}P intensity), and after 17 days this was the major species in solution (ca. 60%), the remainder being [Pt(C≡CMe)$_2$(dppm)].

[Pt(C≡CMe)$_2$(depm)] and PPh$_3$. [Pt(C≡CMe)$_2$(depm)] (7.0 mg, 0.015 mmol) was dissolved in CD_2Cl_2 (0.4 mL). After 6 days at room-temperature ^{31}P and ^1H NMR examination revealed no change in the solution. PPh_3 (0.5 mg, 0.0019 mmol) was added and, after 24 h, ^{31}P NMR examination revealed the presence of both *cis,cis*- and *cis,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$)]. After 6 days a small amount of *trans,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$] was also present. After 3 weeks at room temperature the solution contained only *cis,cis*-, *cis,trans*-, and *trans,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$] in an approximate ratio of 3:6:1.

[Pt$_2$Cl$_2$(depm)$_2$] and Hg(C≡CMe)$_2$. [Pt$_2$Cl$_2$(depm)$_2$] (10.0 mg, 0.012 mmol) and Hg(C≡CMe)$_2$ (6.6 mg, 0.024 mmol) were mixed in CD_2Cl_2 (0.4 mL) under an atmosphere of N_2. After 15 min all of the Hg(C≡CMe)$_2$ had dissolved and a fine black precipitate had appeared. After the mixture was filtered, $^{31}P\{^1H\}$ and ^1H NMR examination revealed that the major product was *trans,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$] (ca. 80% of the ^{31}P intensity).

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Registry No. [Pt(C≡CMe)$_2$(dppm)], 88690-36-2; [Pt(C≡CMe)$_2$(depm)], 94249-25-9; [Pt(C≡CMe)$_2$(dippm)], 94249-26-0; *cis,cis*-[Pt$_2$(C≡CMe)$_4$(dmpm)$_2$], 94249-27-1; *trans,trans*-[Pt$_2$(C≡CMe)$_4$(dppm)$_2$], 84365-28-6; *cis,cis*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$], 94249-28-2; *cis,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$], 94345-77-4; *trans,trans*-[Pt$_2$(C≡CMe)$_4$(depm)$_2$], 94345-78-5; [PtCl$_2$(depm)], 91491-50-8; [PtCl$_2$(dippm)], 94278-50-9; [PtCl$_2$(dppm)], 52595-94-5; [Pt$_2$Cl$_4$(dmpm)$_2$], 94249-29-3; dppm, 2071-20-7; Hg(C≡CMe)$_2$, 64705-15-3; PPh_3, 603-35-0; MeC≡CH, 74-99-7.