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Supplementary Material Available: Calculated hydrogen coordinates (Table V), anisotropic thermal parameters (Table VI), and observed and calculated structure factors for **3** (Table VII) (21 pages). Ordering information is given on any current masthead page.

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Platinum(II) Complexes of Unsymmetrical, Potentially Bidentate Ligands

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The reactions of a series of unsymmetrical, potentially bidentate ligands $Ph_2P(CH_2)_nX$ (n = 2, X = OMe, NMe_2, SMe; n = 3, X = NMe_2) with $[PtX_2(cod)]$ (X = Cl, I) are described. The tendency of the ligand to bond to the metal in a bidentate fashion is dependent on the nature of the weak donor, and on the size of the chelate ring formed. Halide abstraction by Ag^+ promotes coordination of the ether function to yield $[PtCl(Ph_2PCH_2CH_2OMe)_2]^+$ and $[Pt(Ph_2PCH_2CH_2OMe)_2]^{2+}$. Reactions of the former with a number of weak donor ligands have been studied by $^{31}P\{^1H\}$ NMR spectroscopy. Complex mixtures are obtained with $Ph_2PCH_2CH_2SMe$, and the involvement of ion-paired species is suggested in this case.

Introduction

The use of transition-metal complexes to catalyze transformations involving unsaturated organic substrates such as olefins or acetylenes is widespread, yet the stability constants for the formation of metal–olefin and –acetylene complexes are generally low.[1] Thus, in order to obtain greater catalytic activities, complexes containing weak donor ligands that may be readily displaced by the unsaturated species have been employed.[2] The idea of preparing low-valent transition-metal complexes containing mixed bidentate ligands, which exhibit one strong and one weak donor function, is one that has been advanced in the last few years.[3] The utility of such ligands in terms of homogeneous catalysis lies in the susceptibility of the weak donor to displacement by a substrate molecule, whereas the chelate effect confers additional stability on the catalyst precursor in the absence of the substrate.

In this paper we report the preparation of a series of such ligands, $Ph_2P(CH_2)_nX$ (n = 2, X = OMe, NMe_2, SMe; n = 3, X = NMe_2), and the formation and reactions of their platinum(II) complexes. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies have been employed to characterize the ligands, and the solution chemistry of the platinum(II) complexes has been studied with $^{31}P\{^1H\}$ NMR spectroscopy.

Experimental Section

The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 25.1 and 40.2 MHz, respectively, on a JEOL FX-100 spectrometer operating in the Fourier transform mode and were obtained for $CDCl_3$ solutions unless otherwise stated. Infrared spectra were measured from KBr pellets using a Perkin-Elmer 521 spectrophotometer. Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

The compounds $ClCH_2CH_2OMe$, $Cl(CH_2)_nNMe_2\cdot HCl$ (n = 2, 3), and $ClCH_2CH_2SMe$ were obtained from Aldrich. The free amines were generated by treating the hydrochlorides with KOH, extracting with ether, and drying over Na_2SO_4. The ether and thioether were used without further purification. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use.

2-(Diphenylphosphino)ethyl Methyl Ether, $Ph_2PCH_2CH_2OMe$.[4] 2-Chloroethyl methyl ether (10.3 g, 0.11 mol) was added dropwise to a solution of $LiPPh_2$ (24 g, 0.12 mol) (prepared from lithium and chlorodiphenylphosphine) in dry THF (250 mL) under nitrogen at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 30 min. Deoxygenated water (100 mL) was added slowly, the organic layer was separated, and the solvent was evaporated. The residual viscous oil was distilled under reduced pressure (bp 164 °C (0.5 torr)) to give $Ph_2PCH_2CH_2OMe$ as a colorless oil; yield 15.0 g (56%).

The following were prepared analogously: $Ph_2PCH_2CH_2NMe_2$ (bp 160 °C (0.5 torr)), obtained as a colorless oil in 51% yield; $Ph_2P(CH_2)_3NMe_2$ (bp 174–180 °C (0.5 torr)), obtained as a colorless oil in 72% yield; $Ph_2PCH_2CH_2SMe$ (bp 148–154 °C (0.5 torr)), obtained as a colorless oil that solidified on standing, in 66% yield.

***cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$.** To a solution containing $Ph_2PCH_2CH_2OMe$ (1.30 g, 5.33 mmol) in chloroform (50 mL) was added $[PtCl_2(cod)]$ (1.00 g, 2.67 mmol). The mixture was stirred for 15 min, and diethyl ether was added slowly to initiate crystallization. The product was filtered and washed with ether (50 mL) to give *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$ as colorless crystals: yield, 1.60 g (79%); mp 192 °C. Anal. Calcd for $C_{30}H_{34}Cl_2O_2P_2Pt$: C, 47.77; H, 4.53. Found: C, 47.70; H, 4.63.

***cis*-$[PtCl_2[Ph_2P(CH_2)_3NMe_2]_2]$.** This complex was compared as above and isolated as pale yellow crystals: yield, 74%; mp >200 °C. Anal. Calcd for $C_{34}H_{44}Cl_2N_2P_2Pt$: C, 50.76; H, 5.48. Found: C, 50.53; H, 5.41.

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(1) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.

(2) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134. Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299. Sen, A.; Lai, T. W. *Organometallics* **1982**, *1*, 415.

(3) See, for example: Roundhill, D. M.; Bechtold, R. A.; Roundhill, S. G. N. *Inorg. Chem.* **1980**, *19*, 284. Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 299. Sanger, A. R.; Day, R. W. *Inorg. Chim. Acta* **1982**, *62*, 99. Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.

(4) Knebel, W. J.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 713. Smith, R. T.; Baird, M. C. *Inorg. Chim. Acta* **1982**, *62*, 135. Ross, E. P.; Dobson, G. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2363. McEwen, W. E.; Janes, A. B.; Knapczyk, J. W.; Kyllingstad, W. S.; Shore, S.; Smith, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 7304.

(5) Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30.

0020-1669/84/1323-4064$01.50/0

Table I. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR Parameters of the Ligands $Ph_2P(CH_2)_nX$

ligand	δ(C)[a]	J(P,C), Hz	δ(P)[b]
$Ph_2PCH_2CH_2OCH_3$	28.6	12	−22.6
	69.7	24	
	58.4		
$Ph_2PCH_2CH_2N(CH_3)_2$	26.3	12	−20.3
	56.0	22	
	44.9		
$Ph_2PCH_2CH_2CH_2N(CH_3)_2$	25.5	11	−17.0
	23.7	16	
	60.4	14	
	45.0		
$Ph_2PCH_2CH_2SCH_3$	29.2	14	−16.7
	30.6	21	
	15.4		

[a] Chemical shifts are relative to internal Me_4Si, positive shifts representing deshielding; the aromatic resonances are not given. [b] Chemical shifts are relative to external H_3PO_4, positive shifts representing deshielding.

$[PtCl(Ph_2PCH_2CH_2NMe_2)_2]Cl$. To a chloroform solution containing $Ph_2PCH_2CH_2NMe_2$ (0.669 g, 2.60 mmol) was added $[PtCl_2(cod)]$ (0.480 g, 1.28 mmol), and the mixture was stirred for 15 min. After precipitation with ether, the product was filtered and washed with ether to give $[PtCl(Ph_2PCH_2CH_2NMe_2)_2]Cl$ as pale yellow crystals: yield 0.715 g (71%); mp 198 °C.

$[PtCl(Ph_2PCH_2CH_2OMe)_2]ClO_4$. To a chloroform solution containing *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$ (2.05 g, 2.72 mmol) was added $AgClO_4$ (0.55 g, 2.66 mmol). The mixture was stirred for 1 h and filtered to remove the precipitated AgCl. Ether was added slowly to the filtrate to initiate crystallization. Filtration, followed by washing with ether (50 mL), gave the product as colorless crystals: yield 1.60 g (72%); mp 208–210 °C. Anal. Calcd for $C_{30}H_{34}Cl_2O_6P_2Pt$: C, 44.04; H, 4.18. Found: C, 43.86; H, 4.12.

***cis*-$[Pt(Ph_2PCH_2CH_2OMe)_2][BF_4]_2$.** A chloroform solution of *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$ (0.796 g, 1.06 mmol) was treated with excess $AgBF_4$ (>2 mol equiv), and the mixture was stirred for 1 h. Following filtration to remove precipitated AgCl, ether was added to the solution. The product was filtered and washed with ether to give *cis*-$[Pt(Ph_2PCH_2CH_2OMe)_2][BF_4]_2$ as colorless crystals: yield, 0.578 g (64%); mp >200 °C. Anal. Calcd for $C_{30}H_{34}B_2F_8O_2P_2Pt$: C, 42.03; H, 3.99. Found: C, 42.02; H, 3.99.

***trans*-$[PtCl(CO)(Ph_2PCH_2CH_2OMe)_2]ClO_4$.** Carbon monoxide was passed through a chloroform solution of $[PtCl(Ph_2PCH_2CH_2OMe)_2]ClO_4$ for 30 min, whereupon quantitative product formation was indicated by $^{31}P\{^1H\}$ NMR spectroscopy. On standing, *trans*-$[PtCl(CO)(Ph_2PCH_2CH_2OMe)_2]ClO_4$ precipitated as a white solid: mp 206 °C dec; $\nu(CO)$ 2090 cm^{-1}.

All other reactions were performed in NMR tubes, and the products were examined in situ.

Results and Discussion

Preparation of the Ligands. Two methods were employed for the preparation of the ligands, as depicted in eq 1 and 2.

$$Ph_2PCl + 2Li \xrightarrow{-LiCl} Ph_2PLi \xrightarrow[-LiCl]{Cl(CH_2)_nX} Ph_2P(CH_2)_nX \quad (1)$$

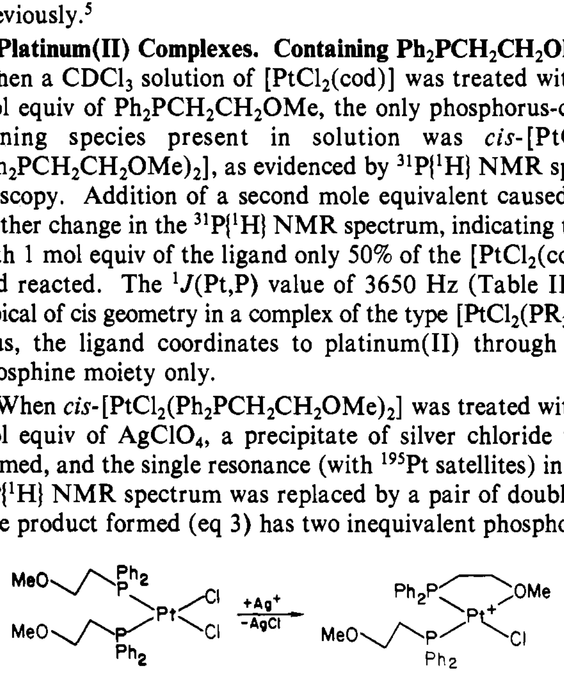
$$Ph_3P + 2Li \rightarrow PhLi + Ph_2PLi \xrightarrow[2.\ Cl(CH_2)_nX]{1.\ t\text{-}BuCl} Ph_2P(CH_2)_nX \quad (2)$$

In our hands the former method has proved the more successful, since it avoids the generation, and subsequent destruction, of phenyllithium. Also, we have experienced some oxidation of the phosphine moiety when the second method has been employed.

The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic data for the ligands are given in Table I. The $^{31}P\{^1H\}$ NMR spectra each exhibit a single resonance around δ(P) −20. The $^{13}C\{^1H\}$ NMR spectra, in addition to signals in the range δ(C) 128–135 due to the diphenylphosphino moiety, exhibit well-defined singlet and doublet resonances due to the alkyl chain and terminal methyl group(s). The methyl carbons give rise to singlets, which are shifted downfield in the O- and N-containing ligands. The methylene carbon resonances are doublets, due to coupling to ^{31}P, with $^2J(P,C)$ being larger than $^1J(P,C)$ (or $^3J(P,C)$ in the case of $Ph_2P(CH_2)_3NMe_2$), as has been found previously.[5]

Platinum(II) Complexes. Containing $Ph_2PCH_2CH_2OMe$. When a $CDCl_3$ solution of $[PtCl_2(cod)]$ was treated with 1 mol equiv of $Ph_2PCH_2CH_2OMe$, the only phosphorus-containing species present in solution was *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$, as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. Addition of a second mole equivalent caused no further change in the $^{31}P\{^1H\}$ NMR spectrum, indicating that with 1 mol equiv of the ligand only 50% of the $[PtCl_2(cod)]$ had reacted. The $^1J(Pt,P)$ value of 3650 Hz (Table II) is typical of cis geometry in a complex of the type $[PtCl_2(PR_3)_2]$; thus, the ligand coordinates to platinum(II) through the phosphine moiety only.

When *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$ was treated with 1 mol equiv of $AgClO_4$, a precipitate of silver chloride was formed, and the single resonance (with ^{195}Pt satellites) in the $^{31}P\{^1H\}$ NMR spectrum was replaced by a pair of doublets. The product formed (eq 3) has two inequivalent phosphorus atoms in mutually cis positions. The large downfield shift of one phosphorus center is typical of a phosphino group that is part of a five-membered chelate ring,[6] and the $^1J(Pt,P)$ value



(3)

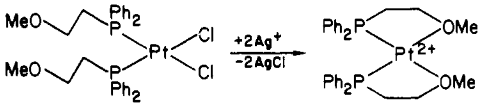
Table II. $^{31}P\{^1H\}$ NMR Parameters of the Platinum(II) Complexes Containing the PC_2O, PC_2N, and PC_3N Ligands[a]

complex	δ(P$_A$)[b]	$^1J(Pt,P_A)$, Hz	δ(P$_B$)[b]	$^1J(Pt,P_B)$, Hz	$^2J(P_A,P_B)$, Hz
cis-$[PtCl_2(PC_2O)_2]$	4.6	3650			
$[PtCl(PC_2O)(PC_2O)]ClO_4$	2.7	4165	36.3[c]	3630	15
cis-$[Pt(PC_2O)_2][BF_4]_2$	19.4	4220			
trans-$[PtCl(CO)(PC_2O)_2]ClO_4$	14.7	2010			
cis-$[PtCl(py)(PC_2O)_2]ClO_4$	6.6	3190	−1.7[c]	3625	18
cis-$[PtCl(SMe_2)(PC_2O)_2]ClO_4$	11.3	3190	5.6[c]	3565	17
$[PtCl(PC_2N)(PC_2N)]Cl$	−1.0	3200	34.8[c]	3680	17
cis-$[PtCl_2(PC_3N)_2]$	9.0	3650			
$[PtCl(PC_3N)(PC_3N)]BF_4$	4.4	3215	7.3[c]	3765	17

[a] $PC_2O = Ph_2P(CH_2)_2OCH_3$; $PC_2N = Ph_2P(CH_2)_2N(CH_3)_2$; $PC_3N = Ph_2P(CH_2)_3N(CH_3)_2$. [b] Chemical shifts are relative to external H_3PO_4, positive shifts representing deshielding. [c] Trans to Cl.

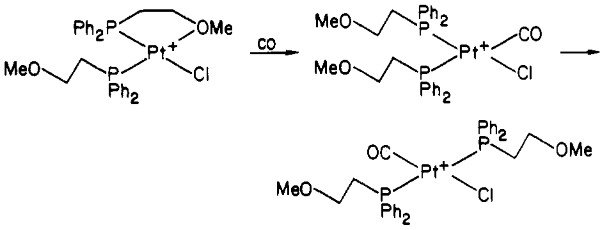
is still indicative of a phosphine trans to chlorine. The larger one-bond coupling constant (4165 Hz) for the other phosphorus atom is expected for a tertiary phosphine lying trans to a weak donor such as an ether.[7]

Treatment of *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$ with 2 mol equiv of $AgBF_4$ (or excess $AgBF_4$) yielded the dication, in which both ligands are chelating. The ${}^1J$ (Pt,P) value (Table II) indicates that the two phosphino moieties lie trans to the ether functions, giving an overall cis geometry (eq 4). Addition of excess $Et_4N^+Cl^-$ to a solution of either the mono- or dication resulted in immediate regeneration of the neutral complex, *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$.



(4)

It is clear that the Pt–O interaction is relatively weak, being formed only when a vacant site is created by halide abstraction, so it was of interest to determine whether other relatively weak donor molecules would be capable of rupturing the Pt–O bond and forming new complexes. When $[PtCl(Ph_2PCH_2CH_2OMe)_2]ClO_4$ was treated with carbon monoxide, reaction occurred immediately to yield *trans*-$[PtCl(CO)(Ph_2PCH_2CH_2OMe)_2]ClO_4$, which readily precipitated from solution. The product exhibits an intense infrared absorption at 2090 cm^{-1}, and the ${}^1J$(Pt,P) value is typical[8] of complexes of the type *trans*-$[PtCl(CO)(PR_3)_2]^+$. Its formation is likely to proceed by displacement of the ether function, followed by isomerization of the resulting cis complex (eq 5).[9]

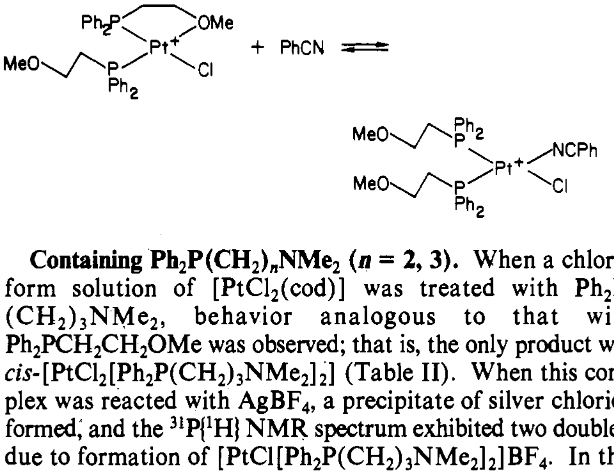


(5)

Analogous treatment of the dication, however, resulted only in decomposition, this no doubt being due to the potentially unfavorable situation where four π-accepting ligands would be required to occupy the coordination sphere of a dipositive ion. In particular, dipositive platinum(II) ions containing two carbonyl ligands, $[Pt(CO)_2L_2]^{2+}$, are unknown.

When ethylene was bubbled through a chloroform solution of $[PtCl(Ph_2PCH_2CH_2OMe)_2]ClO_4$ for 48 h, no new species could be detected by ${}^{31}P\{{}^1H\}$ NMR spectroscopy, and the complex was recovered unchanged. Similarly, addition of methanol or tetrahydrofuran to such a solution caused no change in the ${}^{31}P\{{}^1H\}$ NMR spectrum. Thus, as expected, a simple ether such as THF is unable to displace the ether function of the chelating ligand. Addition of pyridine or dimethyl sulfide, on the other hand, did result in displacement of the ether function, but, in contrast to the reaction with CO, it is the cis isomer that is formed. In each case the ${}^{31}P\{{}^1H\}$ NMR spectrum exhibits two doublets (with ${}^{195}Pt$ satellites), both of which appear at relatively high field since neither ligand is chelating.[6] The ${}^2J$(P,P) values are typical of mutually cis phosphines, whereas the one-bond coupling constants are indicative of a phosphine trans to chlorine and a phosphine trans to the somewhat higher trans-influence ligands C_5H_5N and Me_2S.[7,10]

A less straightforward situation arose when benzonitrile was added to a $CDCl_3$ solution of $[PtCl(Ph_2PCH_2CH_2OMe)_2]ClO_4$. The ${}^{31}P\{{}^1H\}$ NMR spectrum of such a solution at ambient temperature exhibited a sharp doublet at δ(P) 2.6 (${}^1J$(Pt,P) = 4130 Hz, ${}^2J$(P,P) = 17 Hz) and a broad resonance at δ(P) 33.7 (${}^1J$(Pt,P) = ca. 3600 Hz, ${}^2J$(P,P) not observed). When the mixture was cooled to –60 °C, the broad resonance sharpened and the spectrum took on the appearance of that previously observed for $[PtCl(Ph_2PCH_2CH_2OMe)_2]ClO_4$. It may be deduced, therefore, that an exchange process occurs at ambient temperature, most likely involving reversible displacement of the ether function by benzonitrile (eq 6). This exchange may be frozen out at –60 °C, at which temperature the reaction depicted in eq 6 lies completely to the left.



(6)

Containing $Ph_2P(CH_2)_nNMe_2$ (n = 2, 3). When a chloroform solution of $[PtCl_2(cod)]$ was treated with $Ph_2P(CH_2)_3NMe_2$, behavior analogous to that with $Ph_2PCH_2CH_2OMe$ was observed; that is, the only product was *cis*-$[PtCl_2[Ph_2P(CH_2)_3NMe_2]_2]$ (Table II). When this complex was reacted with $AgBF_4$, a precipitate of silver chloride formed, and the ${}^{31}P\{{}^1H\}$ NMR spectrum exhibited two doublets due to formation of $[PtCl[Ph_2P(CH_2)_3NMe_2]_2]BF_4$. In this instance the chelating ligand forms a six-membered ring, so the ${}^{31}P$ resonance is not shifted downfield.[6] The two phosphino moieties occupy mutually cis positions, and the two ${}^1J$(Pt,P) values are typical of a phosphine trans to chlorine (3765 Hz) and trans to an amine (3215 Hz), respectively.[10] Even on treatment wtih excess $AgBF_4$, however, the complex could not be induced to react further. This may be due to the relatively insoluble nature of $[PtCl[Ph_2P(CH_2)_3NMe_2]_2]BF_4$, but it might alternatively be due to an intrinsic difficulty associated with forming two six-membered chelate rings for this particular ligand.

By contrast, addition of $Ph_2PCH_2CH_2NMe_2$ to a chloroform solution of $[PtCl_2(cod)]$ resulted in formation of the $[PtCl(Ph_2PCH_2CH_2NMe_2)_2]^+$ cation, without added Ag^+, and the isolated product was $[PtCl(Ph_2PCH_2CH_2NMe_2)_2]Cl$. Thus, the amino function is a sufficiently good nucleophile to displace chloride when a five-membered chelate ring will result, but not when the product will contain a six-membered ring. This provides an excellent example of how the stability of a square-planar transition-metal complex is determined by the "bite" of the chelating ligand.

Containing $Ph_2PCH_2CH_2SMe$. The reactions of $[PtCl_2(cod)]$ with $Ph_2PCH_2CH_2SMe$ proved to be much more complicated, with mixtures of products often resulting. We therefore carried out analogous reactions with $[PtI_2(cod)]$ and found that the products formed, as well as their relative proprotions, are affected by the nature of the halide. The results of the reactions of $[PtX_2(cod)]$ (X = Cl, I) with $Ph_2PCH_2CH_2SMe$ are presented in Table III.

While this work was in progress, a paper appeared[11] that described the reactions of platinum(II) complexes with

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(6) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(7) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(8) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 427.

(9) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.

(10) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 434.

(11) Sanger, A. R. *Can. J. Chem.* **1983**, *61*, 2214.

Table III. $^{31}P\{^1H\}$ NMR Parameters of the Products of the Reactions of $[PtX_2(cod)]$ (X = Cl, I) with $Ph_2PCH_2CH_2SMe$

reactants	$\delta(P)^a$	$^1J(Pt,P)$, Hz	products
$[PtCl_2(cod)] + Ph_2PCH_2CH_2SMe$	39.5	3680	$[PtCl_2(Ph_2PCH_2CH_2SMe)]$
$[PtCl_2(cod)] + 2Ph_2PCH_2CH_2SMe$	35.1	3295	A
	46.0 (d)^b	3535	B
	16.5 (d)^b	3170	
	43.6 (d)^b	3550	C
	11.6 (d)^b	3120	
$[PtCl_2(cod)] + 2PC_2S + AgBF_4$ (excess)	45.5	3090	$[Pt(Ph_2PCH_2CH_2SMe)_2][BF_4]_2$
$[PtI_2(cod)] + Ph_2PCH_2CH_2SMe$	47.9	3400	$[PtI_2(Ph_2PCH_2CH_2SMe)]$
$[PtI_2(cod)] + 2Ph_2PCH_2CH_2SMe$	36.2	3215	A′
	−17.3		$Ph_2PCH_2CH_2SMe$
$[PtI_2(cod)] + 2PC_2S + AgBF_4$	38.5	3180	A′
	52.4 (d)^b	3330	B′
	10.9 (d)^b	3140	
	49.9 (d)^{b,c}	3330	C′
	6.8 (d)^{b,c}	3245	
	48.2^c	3400	$[PtI_2(Ph_2PCH_2CH_2SMe)]$
$[PtI_2(cod)] + 2PC_2S + AgBF_4$ (excess)	45.5	3100	$[Pt(Ph_2PCH_2CH_2SMe)_2][BF_4]_2$

[a] Chemical shifts are relative to external H_3PO_4, positive shifts representing deshielding. [b] $^2J(P,P) = 15$ Hz. [c] Trace amount present.

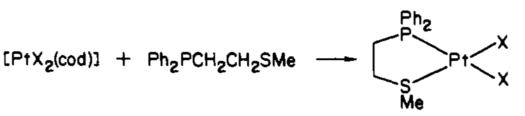
$Ph_2PCH_2CH_2SPh$. These reactions were apparently simple and are summarized in eq 7 and 8. The $^{31}P\{^1H\}$ NMR spectra

$$K_2PtCl_4 + Ph_2PCH_2CH_2SPh \rightarrow \text{“}\textit{trans}\text{-}[PtCl_2(Ph_2PCH_2CH_2SPh)]\text{”} \rightarrow \textit{cis}\text{-}[PtCl_2(Ph_2PCH_2CH_2SPh)] \quad (7)$$

$$[PtCl_2(NCPh)_2] + 2Ph_2PCH_2CH_2SPh \rightarrow \textit{cis}\text{-}[PtCl_2(Ph_2PCH_2CH_2SPh)_2] \xrightarrow{NaBPh_4} [PtCl(Ph_2PCH_2CH_2SPh)_2]BPh_4 \xrightarrow{NaBPh_4\ (excess)} [Pt(Ph_2PCH_2CH_2SPh)_2][BPh_4]_2 \quad (8)$$

were obtained at −50 °C and indicated the presence of only one species in each case. In our system the reactions have not proved to be so straightforward, and the results appear to be consistent with the methyl thioether moiety being a better nucleophile than its phenyl analogue (vide infra).

When a chloroform solution of $[PtCl_2(cod)]$ was treated with 1 mol equiv of $Ph_2PCH_2CH_2SMe$, displacement of the diolefin occurred to yield $[PtCl_2(Ph_2PCH_2CH_2SMe)]$, in which the ligand is chelated. With $[PtI_2(cod)]$ a similar reaction took place, the product exhibiting a large downfield chemical shift in its $^{31}P\{^1H\}$ NMR spectrum, typical of a five-membered chelate ring,[6] and a somewhat smaller $^1J(Pt,P)$ value for the phosphino moiety trans to iodine (Table III). These reactions are depicted in eq 9. Additon of a second mole equivalent of the ligand to $[PtCl_2(Ph_2PCH_2CH_2SMe)]$ or, alternatively, reaction of $[PtCl_2(cod)]$ with 2 mol equiv of $Ph_2PCH_2CH_2SMe$ gave a mixture of three products (Table III). One of these, species A, exhibited a slightly broadened singlet (with ^{195}Pt satellites) in the $^{31}P\{^1H\}$ NMR spectrum, while species B and C each gave rise to a pair of doublets, the corresponding high-field and low-field signals having remarkably similar one-bond coupling constants. Treatment of this mixture with 1 mol equiv of $AgBF_4$ did not produce any change in the number of species present, but the signals due to species B increased in intensity relative to those of A and C. Addition of excess $AgBF_4$ caused complete conversion to $[Pt(Ph_2PCH_2CH_2SMe)_2][BF_4]_2$, in which the phosphino moieties occupy mutually cis positions. The values of $\delta(P)$ and $^1J(Pt,P)$ are almost identical with those obtained for the phenyl thioether analogue.[11]



(9)

Species B and C exhibit remarkably similar spectroscopic parameters. Both complexes contain two inequivalent phosphorus atoms in mutually cis positions, where one is part of a five-membered chelate ring, whereas the second ligand is bonded to the metal through phosphorus only (Table III). Such a pattern is precisely what would be expected for the $[PtCl(Ph_2PCH_2CH_2SMe)_2]^+$ cation, so this species may be accounted for by either B or C. The identity of the other is uncertain, although the spectroscopic data rule out all but the most closely related structure.

When a second mole equivalent of $Ph_2PCH_2CH_2SMe$ was added to a $CDCl_3$ solution of $[PtI_2(Ph_2PCH_2CH_2SMe)]$, the $^{31}P\{^1H\}$ NMR spectrum indicated the presence of the free ligand and a new platinum-containing species A′ (Table III), the latter being closely related to A (vide infra). On addition of $AgBF_4$ the latter persisted,[12] and a species B′, which exhibited two doublets in the $^{31}P\{^1H\}$ NMR spectrum, was formed, with parameters consistent with those of the $[PtI(Ph_2PCH_2CH_2SMe)_2]^+$ cation. Also, minor amounts of $[PtI_2(Ph_2PCH_2CH_2SMe)]$ and a species C′, which exhibited high- and low-field doublet resonances, were detected; as in the chloride case, the origin of the second pair of doublets is unknown. With excess $AgBF_4$ the $^{31}P\{^1H\}$ NMR spectrum indicated quantitative formation of $[Pt(Ph_2PCH_2CH_2SMe)_2][BF_4]_2$ had occurred, the spectrum being identical with that obtained for the chloride case, which provides further evidence that this formulation is correct.

When a $CDCl_3$ solution containing species A–C was cooled to −50 °C, the intensities of the signals due to B increased and the resonance due to A became sharper and moved downfield until it overlapped the low-field doublet of species C. In addition, a sharp singlet at $\delta(P)$ 40.4, due to $[PtCl_2(Ph_2PCH_2CH_2SMe)]$, became apparent. Species A could be generated independently by treating a chloroform solution of $[PtCl_2(cod)]$ with 3 mol equiv of $Ph_2PCH_2CH_2SMe$; a colorless material precipitated that, when redissolved in $CDCl_3$ exhibited a $^{31}P\{^1H\}$ NMR spectrum identical with that of A. Cooling this solution to −50 °C caused the signal to shift to $\delta(P)$ 44.1 and the one-bond coupling constant to decrease to 3215 Hz. These values are approaching those for $[Pt(Ph_2PCH_2CH_2SMe)_2]^{2+}$, and we suggest that species A is this dication with one or two loosely associated chloride ions.

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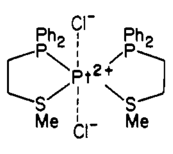
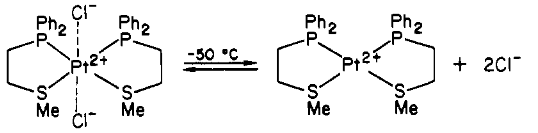
(12) The minor changes in chemical shift and coupling constant of A′ shown in Table III are likely due to temperature fluctuation. The effect of temperature on the spectroscopic parameters is described in the text.



A

Exchange of chloride apparently occurs, causing broadening of the ^{31}P resonance, at ambient temperature. At low temperature the equilibrium position more closely resembles a situation involving free ions (eq 10), a result for which there is considerable precedent.[13,14] A similar situation is found to prevail for A′, the iodo analogue of species A.



(10)

We have investigated the solvent and temperature dependences of A and A′ (Table IV), and these studies support their formulations as ion-paired complexes. Species A was generated separately (vide supra), and its temperature dependence in $CDCl_3$ solution was studied, whereas the other investigations were of A–C or A′–C′ mixtures, which were obtained by addition of 2 mol equiv of $Ph_2PCH_2CH_2SMe$ to the appropriate solution of $[PtX_2(cod)]$ (X = Cl, I) or by introduction of $Et_4N^+Cl^-$ or n-$Bu_4N^+I^-$ into a solution of $[Pt(Ph_2PCH_2CH_2SMe)_2][BF_4]_2$ (generated from $[PtCl_2(cod)]$ and 2 mol equiv of $Ph_2PCH_2CH_2SMe$ followed by excess $AgBF_4$). At low temperature in chloroform solution the $^{31}P\{^1H\}$ NMR spectrum of A or A′ approximates that of the $[Pt(Ph_2PCH_2CH_2SMe)_2]^{2+}$ cation, whereas raising the temperature or increasing the polarity of the solvent causes an upfield shift of the resonance due to A or A′, accompanied by an increase in $^1J(Pt,P)$. In more polar solvents this may be due to increased solvation of the ions.

In contrast to the work of Sanger with the phenyl thioether[11] we do not generate significant amounts of *cis*-$[PtCl_2(Ph_2PCH_2CH_2SMe)_2]$ from the reaction of $[PtCl_2(cod)]$ with 2 mol equiv of $Ph_2PCH_2CH_2SMe$. When $[PtCl_2(cod)]$ in $CDCl_3$ was reacted with 1.75 mol equiv of the ligand at −50 °C, then briefly warmed to ambient temperature before recording the $^{31}P\{^1H\}$ NMR spectrum at −50 °C, a resonance due to *cis*-$[PtCl_2(Ph_2PCH_2CH_2SMe)_2]$ ($\delta(P)$ 14.0, $^1J(Pt,P)$ = 3685 Hz) was observed in addition to those for $[PtCl_2(Ph_2PCH_2CH_2SMe)]$ and species A–C. After the mixture was allowed to stand at room temperature, or on addition of further $Ph_2PCH_2CH_2SMe$, this resonance diminished in intensity, however. Thus, for platinum:ligand ratios of 1:2, one or both of the methyl thioether moieties are always coordinated, indicating that the methyl thioether function is a stronger nucleophile toward platinum(II) than its phenyl analogue. The dication, $[Pt(Ph_2PCH_2CH_2SMe)_2]^{2+}$, assumes cis geometry exclusively, as does $[Pt(Ph_2PCH_2CH_2OMe)_2]^{2+}$, owing to the disparity between the trans influences of the phosphine and thioether, or ether, moieties,[7] whereas it was found that $[Pt(Ph_2PCH_2CH_2AsPh_2)_2]^{2+}$ exists as two isomers[15] since the trans influence of the arsine more closely approaches that of the tertiary phosphine.

Table IV. Solvent and Temperature Dependences of the $^{31}P\{^1H\}$ NMR Spectra of Species A and A′

		A		A′	
solvent	temp, °C	$\delta(P)^a$	$^1J(Pt,P)$, Hz	$\delta(P)^a$	$^1J(Pt,P)$, Hz
$CHCl_3$	−50	44.1	3215	43.2	3150
$CHCl_3$	+20	35.1	3295	36.2	3215
$CHCl_3$	+60	30.5	3330		
$CHCl_3/(CH_3)_2CO$	+20	32.0	3325		
$(CH_3)_2CO$	+20	26.3	3345	30.2	3245
CH_3CN	+20			30.9	3235

[a] Chemical shifts are relative to external H_3PO_4, positive shifts representing deshielding.

The above results show that the chelating ability of these potentially bidentate ligands is dependent on both the nature of the "weak" donor and the size of the chelate ring that will be formed. The stability of the complexes formed by $Ph_2PCH_2CH_2OMe$, and the facile displacement of the ether function in solution, suggests that they may prove to be useful homogeneous catalyst precursors for olefin hydrogenation or hydroformylation, and this possibility is being investigated.

Acknowledgment. Thanks are expressed to Johnson Matthey for a generous loan of platinum salts, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corp. and the University of Missouri Weldon Spring Fund for support of this work.

Registry No. $Ph_2PCH_2CH_2OMe$, 68899-50-3; $Ph_2PCH_2CH_2NMe_2$, 29679-67-2; $Ph_2P(CH_2)_3NMe_2$, 961-04-6; $Ph_2PCH_2CH_2SMe$, 20859-51-2; $ClCH_2CH_2OMe$, 627-42-9; $ClCH_2CH_2NMe_2$, 107-99-3; $Cl(CH_2)_3NMe_2$, 109-54-6; $ClCH_2CH_2SMe$, 542-81-4; $LiPPh_2$, 4541-02-0; *cis*-$[PtCl_2(Ph_2PCH_2CH_2OMe)_2]$, 92763-45-6; $[PtCl_2(cod)]$, 12080-32-9; *cis*-$[PtCl_2[Ph_2P(CH_2)_3NMe_2]_2]$, 92763-46-7; $[PtCl(Ph_2PCH_2CH_2NMe_2)_2]Cl$, 92763-47-8; $[PtCl(Ph_2PCH_2CH_2OMe)_2]ClO_4$, 92763-49-0; *cis*-$[Pt(Ph_2PCH_2CH_2OMe)_2][BF_4]_2$, 92763-51-4; *trans*-$[PtCl(CO)(Ph_2PCH_2CH_2OMe)_2]ClO_4$, 92763-53-6; *cis*-$[PtCl(NCPh)(Ph_2PCH_2CH_2OMe)_2]^+$, 92786-74-8; $[PtCl(Ph_2PCH_2CH_2SMe)_2]^+$, 92763-64-9; $[PtI(Ph_2PCH_2CH_2SMe)_2]^+$, 92763-65-0; *cis*-$[PtCl(py)(Ph_2PCH_2CH_2OMe)_2]ClO_4$, 92763-55-8; *cis*-$[PtCl(SMe_2)(Ph_2PCH_2CH_2OMe)_2]ClO_4$, 92763-57-0; $[PtCl(Ph_2P(CH_2)_3NMe_2)(Ph_2P(CH_2)_3NMe_2)_2]BF_4$, 92763-59-2; $[PtI_2(cod)]$, 12266-72-7; $[Pt(Ph_2PCH_2CH_2SMe)_2][BF_4]$, 92763-62-7; $[PtI_2(Ph_2PCH_2CH_2SMe)]$, 92763-63-8; $[PtCl_2(Ph_2PCH_2CH_2SMe)]$, 92763-60-5; PH_3, 7803-51-2.

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(13) Godleski, S. A.; Gundlach, K. B.; Ho, H. Y.; Keinan, E.; Frolow, F. *Organometallics* **1984**, *3*, 21.

(14) Szwarc, M. "Ions and Ion Pairs in Organic Reactions"; Wiley Interscience: New York, 1972; p 85.

(15) Anderson, G. K.; Davies, J. A.; Schoeck, D. J. *Inorg. Chim. Acta* **1983**, *76*, L251.