Chem. **1979**, *18*, 240-244.
(7) Authier-Martin, M.; Beauchamp, A. L. *Can. J. Chem.* **1977**, *55*, 1213-1217.
(8) Szalda, D.; Marzilli, L. G.; Kistenmacher, T. J. *Biochem. Biophys. Res. Commun.* **1975**, *63*, 601-605.
(9) Bau, R.; Gellert, R. W.; Shiba, J. K. Abstracts, 7th International Conference on Organometallic Chemistry, Venice, Italy, 1975; p 238.
(10) Aoki, K. *Biochim. Biophys. Acta* **1976**, *447*, 379-381.
(11) Sinn, E.; Flynn, C. M.; Martin, R. B. *Inorg. Chem.* **1977**, *16*, 2403-2406.
(12) Clark, G. R.; Orbell, J. D. *Acta Crystallogr., Sect. B*, **1978**, *34*, 1815-1822.
(13) Neidle, S.; Taylor, G. L.; Robins, A. B. *Acta Crystallogr., Sect. B*, **1978**, *34*, 1838-1841.
(14) Lock, C. J. L.; Speranzini, R. A.; Powell, J. *Can. J. Chem.* **1976**, *54*, 53-58.
(15) Goodgame, D. M. L.; Jeeves, I.; Reynolds, C. D.; Skapski, A. C. *Biochem. J.* **1975**, *151*, 467-468.
(16) Singh, P.; Hodgson, D. J. *Biochemistry* **1974**, *13*, 5445-5452.
(17) Furberg, S.; Petersen, C. S.; Romming, C. *Acta Crystallogr.* **1965**, *18*, 313-320.
(18) Arya, S. K.; Yang, J. T. *Biopolymers* **1975**, *14*, 1847-1861, and references cited therein.
(19) (a) Clarke, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 5068-5075. (b) Clarke, M. J.; Buchbinder, M.; Kelman, A. D. *Inorg. Chim. Acta* **1978**, *27*, L87-L88.
(20) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197-204.
(21) (a) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-ray Crystallography", Vol. IV; Kynoch Press: Birmingham, England, 1974; Table 2.1C, pp 61-66. (b) *Ibid.* Table 2.2A, pp 72-98; Table 2.2C, p 102. (c) *Ibid.* Table 2.3.1, pp 149-150.
(22) For a description of the programs used in this structural analysis, see Lewis, D. L.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 143-147.
(23) See paragraph at end of paper regarding supplementary material.
(24) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304-2308.
(25) Phelps, D. W.; Kahn, E. M.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 2486-2490.
(26) Peresie, H. J.; Stanko, J. A. *Chem. Commun.* **1970**, 1674-1675.
(27) Roberts, G. W.; Cummings, S. C.; Cunningham, J. A. *Inorg. Chem.* **1976**, *15*, 2503-2510.
(28) Laing, M. *Acta Crystallogr., Sect. B* **1978**, *34*, 2100-2104.
(29) Morrison, R. M.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1979**, *57*, 135-138.
(30) Pierpont, C. G.; Van Derveer, D. G.; Durland, W.; Eisenberg, R. *J. Am. Chem. Soc.* **1970**, *92*, 4760-4762.
(31) Veal, J. T.; Hodgson, D. J. *Inorg. Chem.* **1972**, *11*, 1420-1424.
(32) Veal, J. T.; Hodgson, D. J. *Acta Crystallogr., Sect. B* **1972**, *28*, 3525-3529, and references cited therein.
(33) Mansy, S.; Frick, J. P.; Tobias, R. S. *Biochim. Biophys. Acta* **1975**, *378*, 319-332.
(34) Clarke, M. J. *Inorg. Chem.* **1977**, *16*, 738-744.
(35) Neubecker, T. A.; Kirksey, S. T.; Chellappa, K. L.; Margerum, D. W. *Inorg. Chem.* **1979**, *18*, 444-448.
(36) (a) Kistenmacher, T. J. *Acta Crystallogr., Sect. B* **1974**, *30*, 1610-1612. (b) Kistenmacher, T. J.; Marzilli, L. G.; Chang, C. H. *J. Am. Chem. Soc.* **1973**, *95*, 5817-5819.
(37) Sorrell, T.; Epps, L. A.; Kistenmacher, T. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1977**, *99*, 2173-2179.
(38) Viswamitra, M. A.; Reddy, B. S.; Lin, G. H.-Y.; Sundralingam, M. *J. Am. Chem. Soc.* **1971**, *93*, 4565-4573.
(39) Bugg, C. E.; Thomas, J. M.; Sundralingam, M.; Rao, S. T. *Biopolymers* **1971**, *10*, 175-219.

Synthesis and ^{31}P NMR Studies of Unsymmetrical *cis*-Diphosphinoalkenes and Their Complexes with Nickel(II), Palladium(II), and Platinum(II)

A. J. Carty,* D. K. Johnson, and S. E. Jacobson

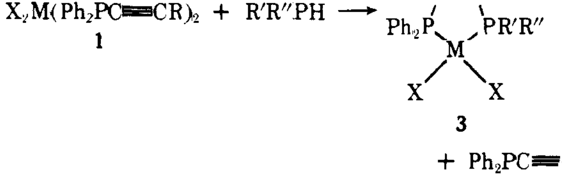
Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1. *Received March 12, 1979*

Abstract: Bis(phosphinoalkyne) complexes *cis*-$Cl_2M(Ph_2PC{\equiv}CR)_2$ (M = Pd, Pt; R = CF_3, Ph, *t*-Bu) undergo a facile 1:1 reaction with secondary phosphines HPR′R″ (R′R″ = Ph, C_2H_4CN; R′ = Et, R″ = Ph) to give stereospecifically the *cis*-1,2-diphosphinoalk-1-ene complexes *cis*-$Cl_2M(Ph_2PCH{=}C(R)PR'R'')$. The uncoordinated diphosphinoalk-1-enes may be obtained by treatment of the corresponding Pt(II) complex with excess cyanide ion. Complexes *cis*-$Cl_2Ni(Ph_2PCH{=}C(R)PR'R'')$ are obtained by reaction of *cis*-$Ph_2PCH{=}C(R)PR'R''$ with anhydrous nickel(II) chloride. The free diphosphinoalk-1-enes and their Ni(II), Pd(II), and Pt(II) complexes are characterized by elemental analysis, mass spectrometry, IR, ^1H NMR, and ^{31}P NMR spectroscopy. Factors affecting ^{31}P chemical shifts, coordination chemical shifts, and P-P couplings in these systems are discussed.

Introduction

Phosphinoalkynes are potentially bidentate ligands but have been shown[1] to coordinate only through phosphorus in the square planar Pd(II) and Pt(II) complexes *cis*-$X_2M(Ph_2PC{\equiv}CR)_2$ (**1**) (R = alkyl, aryl; X = halogen). Although uncoordinated, the alkyne function in these complexes is activated toward such reactions as hydration,[2] hydrogen halide addition,[3] and acetylene coupling.[4] The prospect of an analogous activation toward addition of the P-H moiety led us to examine the reaction of complexes **1** with secondary phosphines.

The base-catalyzed addition of diphenylphosphine to an uncoordinated phosphinoalkyne (eq 1) has been reported[5] to give stereospecifically the *trans*-1,2-bis(phosphino)alk-1-ene (**2**), a molecule which is unable to act as a chelating ligand by virtue of the rigidity of the olefinic backbone.[6] In contrast, our initial studies showed that the addition of secondary phosphines to coordinated phosphinoalkynes in complexes **1** (eq 2) yielded

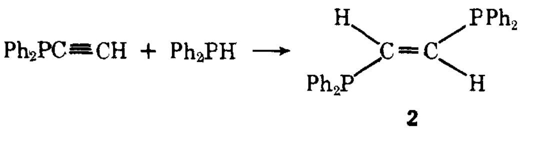


1

3

+ $Ph_2PC{\equiv}CR$ (2)

stereospecifically the *cis*-1,2-diphosphinoalk-1-ene complexes (**3**). Unsaturated, unsymmetrical diphosphines of the type present in complexes **3** are unlikely to be readily obtained by any other route[5,7] and, in view of intense current interest in



(1)

2

rigid diphosphines as ligands,[8] we were prompted to prepare a range of complexes of type **3**.

The incorporation of an unsymmetrical diphosphine into a transition-metal complex makes available additional information concerning the nature of that complex since ^{31}P NMR spectra will generally show a separate resonance for each end of the bidentate ligand and a phosphorus–phosphorus coupling constant ($^2J_{PMP}$) which may be measured directly. This advantage over symmetrical analogues has prompted the development of a number of such ligands, primarily by Grim and co-workers, who have described unsymmetrical bis(phosphorus) ligands of three basic types: (a) those which are unsymmetrical by virtue of the terminal groups [$Ph_2P(CH_2)_nPRR'$, n = 1, 2, 3],[9-12] (b) those in which the backbone is unsymmetrical [$Ph_2P(CH_2)_nOPPh_2$, n = 1, 2],[13] and (c) those in which the two phosphorus atoms are in different oxidation states [$Ph_2P(L)CHRPR'R''$, L = O, S].[14-16] King and co-workers[17-21] have also reported the diphosphines $PhP(H)CH_2CH_2PR_2$ (R = H, Me, Ph, neopentyl), $RP(H)CH_2CH_2PH_2$ (R = hexyl, neopentyl), and $Me_2PCH_2CH_2PR_2$ (R = H, Ph), although, with the exception of $Me_2PCH_2CH_2PPh_2$,[22] the coordination chemistry of these species has yet to be described in any detail. A few complexes of related unsymmetrical diphosphines having a saturated two-carbon backbone, for example, $Me_2PCH_2CH_2PR_2$ (R = Et, *i*-Pr) and $Ph_2PCH_2CH_2P(CF_3)_2$, have been described by other workers.[23] To date, the application of these saturated ligands to ^{31}P NMR studies has been mainly confined to the series *cis*-(L-L')M(CO)$_4$ (M = Cr, Mo, W; L-L' = an unsymmetrical diphosphine), presumably reflecting the accessibility of these complexes and the availability of an existing body of $^2J_{PMP}$ data for analogous fluorophosphine species.[24] A recent paper by Wreford and co-workers[23b] on dynamic processes in C_{2v} monocapped trigonal prismatic complexes does, however, demonstrate the potential of ^{31}P NMR studies using unsymmetrical diphosphine derivatives as a probe of stereochemical behavior.

Remarkably little is known of the variation of $^2J_{PMP}$ within the series *cis*-X_2ML_2 (M = Ni, Pd, Pt; L_2 = two monodentate phosphines or a bidentate diphosphine) and in some cases even the limited data which is to be found in the literature appears contradictory. A study of the ^{31}P NMR spectra of complexes **3** was therefore undertaken as these species, by virtue of the steric properties of the diphosphine,[25] remain isostructural and monometallic throughout the wide range of combinations of R, R', R'', X, and M permitted by the synthetic method. They thus seemed well suited to a systematic study of the factors affecting ^{31}P NMR parameters in this group. Additional interest arose from the chance to examine the effects of unsaturation on the abnormally large coordination chemical shifts previously observed for all saturated five-membered chelate rings[13,26] and from the opportunity to investigate further the relative importance of the ligand backbone vs. the metal center in the transmission of P–P couplings within such rings.[12,13,22]

This paper describes the synthesis and characterization of Ni(II), Pd(II), and Pt(II) complexes (**3**) containing nine new unsymmetrical *cis*-1,2-diphosphinoalk-1-ene ligands, including ^{31}P NMR data for the complexes and for the free diphosphines.

Experimental Section

Substrates $Cl_2M(Ph_2PC\equiv CR)_2$ (M = Pd, Pt; R = CF_3, Ph, *t*-Bu) were prepared as described elsewhere.[1,2,27] Diphenylphosphine and bis(2-cyanoethyl)phosphine were purchased from Strem Chemical Co., Andover, Mass. Ethylphenylphosphine was prepared by the method of Hayter and Humiec.[28] All handling of secondary phosphines and of reaction mixtures containing them was carried out under a nitrogen atmosphere. All solvents were dried and deoxygenated by refluxing over calcium hydride in a stream of nitrogen for several days and were distilled under nitrogen from the desiccant immediately before use.

IR spectra were recorded on a Perkin-Elmer 180 spectrophotometer using Nujol mulls on CsI plates. FT ^{1}H and ^{31}P NMR spectra were obtained at 60 and 24.29 MHz, respectively, on a Bruker WP60 spectrometer, using the deuterium resonance of $CDCl_3$ as an internal lock. Selective proton decoupling experiments were performed on a Bruker WH90 spectrometer. ^{1}H chemical shifts are in parts per million with respect to internal Me_4Si while ^{31}P chemical shifts are in parts per million relative to an external 85% H_3PO_4 standard, shifts to low field of this resonance being shown as positive. ^{31}P NMR spectra were normally recorded under conditions of broad band proton noise decoupling. Mass spectra at 70 eV were run on an AE1-MS-30 spectrometer. Elemental analyses and osmometric molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tenn.

Secondary Phosphine Addition Reactions. Unless otherwise specified, the secondary phosphine addition reactions were carried out under a nitrogen atmosphere up to the point at which the diphosphine complex had formed, subsequent workup and recrystallization being carried out in the air.

***cis*-Dichloro-*cis*-1,2-bis(diphenylphosphino)-3,3,3-trifluoroprop-1-enepalladium(II), $Cl_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$.** A solution of Ph_2PH (0.51 g, 2.72 mmol) in benzene (10 mL) was added to a stirred solution of *cis*-$Cl_2Pd(Ph_2PC\equiv CCF_3)_2$ (1.0 g, 1.36 mmol) in benzene (100 mL), resulting in immediate precipitation of the crude product. After stirring at room temperature for a further 2 h the crude product was filtered off, dried, and recrystallized from hot acetonitrile to give the pure product as a colorless, microcrystalline powder.

***cis*-Dichloro-*cis*-α,β-bis(diphenylphosphino)styrenepalladium(II), $Cl_2Pd(Ph_2PCH{=}C(Ph)PPh_2)$.** A solution of Ph_2PH (0.19 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to a stirred suspension of *cis*-$Cl_2Pd(Ph_2PC\equiv CPh)_2$ (0.73 g, 1.0 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The mixture was stirred and allowed to warm slowly to room temperature. On reaching room temperature only a trace of solid remained undissolved. The reaction mixture was filtered and the pale yellow filtrate was concentrated under vacuum to ca. 15 mL. The subsequent addition of Et_2O (20 mL) resulted in the rapid growth of colorless crystals of the pure complex. These were filtered off, washed with Et_2O (2 × 5 mL), and dried under vacuum.

***cis*-Dichloro-*cis*-α-ethylphenylphosphino-β-diphenylphosphinostyrenepalladium(II), $Cl_2Pd(Ph_2PCH{=}C(Ph)PEtPh)$.** A solution of HPEtPh (0.14 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to a stirred suspension of *cis*-$Cl_2Pd(Ph_2PC\equiv CPh)_2$ (0.73 g, 1.0 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The resulting mixture was allowed to warm to room temperature and after stirring at 25 °C for 1 h almost all of the starting material had been taken into solution. The reaction mixture was filtered and the filtrate concentrated under vacuum to ca. 10 mL. The gradual addition of Et_2O (50 mL) with vigorous stirring gave an amorphous, pale yellow precipitate which was filtered off, washed with Et_2O (2 × 5 mL), and dried. This crude product was then redissolved in CH_2Cl_2 (5 mL) and filtered. The filtrate was diluted with Et_2O until turbid (ca. 10 mL) and on standing at 25 °C for 2 days deposited the pure complex as clumps of very pale yellow crystals. The mother liquor was decanted and the crystals dried at ca. 80 °C (0.1 Torr) for 24 h.

***cis*-Dichloro-*cis*-1-diphenylphosphino-2-bis(2-cyanoethyl)phosphino-3,3,3-trifluoroprop-1-enepalladium(II), $Cl_2Pd[Ph_2PCH{=}C(CF_3)P(C_2H_4CN)_2]$.** A solution of $HP(C_2H_4CN)_2$ (0.14 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of *cis*-$Cl_2Pd(Ph_2PC\equiv CCF_3)_2$ (0.73 g, 1.0 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The reaction mixture was stirred and allowed to warm to 25 °C. Stirring under a brisk N_2 flow was then continued until the volume of the reaction mixture was reduced to ca. 10 mL, at which point the crude complex began to precipitate. Precipitation was completed by the addition of Et_2O (40 mL) and the resulting granular white solid was filtered off, washed with Et_2O (5 mL), and dried under vacuum. Recrystallization from a mixture of CH_2Cl_2 (25 mL) and *n*-hexane (10 mL) gave colorless, fiber-like crystals of the pure complex.

***cis*-Dichloro-*cis*-α-bis(2-cyanoethyl)phosphino-β-diphenylphosphinostyrenepalladium(II), $Cl_2Pd[Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2]$.** A solution of $HP(C_2H_4CN)_2$ (0.14 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to a stirred suspension of *cis*-$Cl_2Pt(Ph_2PC\equiv CPh)_2$ (0.73 g, 1.0 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The reaction mixture was stirred and allowed to warm to room temperature, giving a turbid, yellow solution which was filtered. The filtrate was evaporated to dryness under vacuum and the residue redissolved in a 2:1 EtOH–CH_2Cl_2 mixture (15 mL). With vigorous stirring, Et_2O (20 mL) was added to the resulting yellow solution precipitating the pure product as an amorphous, pale yellow solid. This was filtered off, washed with Et_2O (5 mL), and dried under vacuum.

***cis*-Dichloro-*cis*-1,2-bis(diphenylphosphino)-3,3,3-trifluoroprop-1-eneplatinum(II), $Cl_2Pt(Ph_2PCH{=}C(CF_3)PPh_2)$.** A solution of $HPPh_2$ (0.90 g, 4.86 mmol) in benzene (5 mL) was added to a stirred solution of *cis*-$Cl_2Pt(Ph_2PC{\equiv}CCF_3)_2$ (2.0 g, 2.43 mmol) in benzene (140 mL). Mixing of the two colorless solutions resulted in the immediate formation of a white precipitate. After stirring at 25 °C for a further 2 h the precipitate was filtered off, washed with benzene, and dried. Recrystallization from hot benzonitrile (20 mL) afforded the pure complex in the form of a colorless, microcrystalline powder.

***cis*-Dichloro-*cis*-α,β-bis(diphenylphosphino)styreneplatinum(II), $Cl_2Pt(Ph_2PCH{=}C(Ph)PPh_2)$.** A solution of $HPPh_2$ (0.19 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of *cis*-$Cl_2Pt(Ph_2PC{\equiv}CPh)_2$ (0.84 g, 1.0 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The resulting clear, colorless solution was allowed to warm to room temperature, then was concentrated under vacuum to a volume of ca. 5 mL. The slow addition of Et_2O (25 mL) initiated crystallization of a colorless complex which, after standing overnight to complete crystallization, was filtered off, washed with Et_2O (2 × 5 mL), and dried under vacuum to give the pure product.

***cis*-Dichloro-*cis*-1,2-bis(diphenylphosphino)-3,3-dimethylbut-1-eneplatinum(II), $Cl_2Pt(Ph_2PCH{=}C(t\text{-}Bu)PPh_2)$.** A solution of $HPPh_2$ (0.19 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of *cis*-$Cl_2Pt(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ (0.80 g, 1.0 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The solution was allowed to warm to room temperature, then was concentrated under vacuum to ca. 10 mL. The addition of hexane (15 mL) produced, on standing, well-formed, colorless, rod-like crystals of the pure product which were filtered off, washed with hexane (3 × 5 mL), and dried under vacuum.

***cis*-Dichloro-*cis*-1-diphenylphosphino-2-ethylphenylphosphino-3,3,3-trifluoroprop-1-eneplatinum(II), $Cl_2Pt(Ph_2PCH{=}C(CF_3)PEtPh)$.** A solution of HPEtPh (0.28 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of *cis*-$Cl_2Pt(Ph_2PC{\equiv}CCF_3)_2$ (1.63 g, 2.0 mmol) in CH_2Cl_2 (100 mL) at −78 °C. The resulting straw-colored solution was allowed to warm to room temperature and then was stirred at room temperature for a further 2 h. Concentration under vacuum to a volume of ca. 5 mL and the gradual addition of Et_2O (80 mL) precipitated the crude complex, which was filtered off, washed with Et_2O (5 mL), and dried. Recrystallization from hot acetonitrile (10 mL) afforded colorless crystals of the pure complex.

***cis*-Dichloro-*cis*-α-ethylphenylphosphino-β-diphenylphosphinostyreneplatinum(II), $Cl_2Pt(Ph_2PCH{=}C(Ph)PEtPh)$.** This complex was prepared as colorless crystals from HPEtPh (0.14 g, 1.0 mmol) in CH_2Cl_2 (5 mL) and *cis*-$Cl_2Pt(Ph_2PC{\equiv}CPh)_2$ (0.84 g, 1.0 mmol) in CH_2Cl_2 (50 mL) as described above for $Cl_2Pt(Ph_2PCH{=}C(CF_3)PEtPh)$.

***cis*-Dichloro-*cis*-1-diphenylphosphino-2-ethylphenylphosphino-3,3-dimethylbut-1-eneplatinum(II), $Cl_2Pt(Ph_2PCH{=}C(t\text{-}Bu)PEtPh)$.** Colorless, prismatic crystals were obtained from HPEtPh (0.14 g, 1.0 mmol) in CH_2Cl_2 (5 mL) and *cis*-$Cl_2Pt(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ (0.80 g, 1.0 mmol) in CH_2Cl_2 (50 mL) in similar fashion to $Cl_2Pt(Ph_2PCH{=}C(CF_3)PEtPh$.

***cis*-Dichloro-*cis*-1-diphenylphosphino-2-bis(2-cyanoethyl)phosphino-3,3-dimethylbut-1-eneplatinum(II), $Cl_2Pt[Ph_2PCH{=}C(t\text{-}Bu)P(C_2H_4CN)_2]$.** A solution of $HP(C_2H_4CN)_2$ (0.14 g, 1.0 mmol) in benzene (5 mL) was added to a stirred suspension of *cis*-$Cl_2Pt(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ (0.80 g, 1.0 mmol) in benzene (50 mL). Stirring at room temperature under a brisk flow of nitrogen was continued for 5 h, then the resulting white precipitate of the pure complex was filtered off, washed with benzene (10 mL), and dried under vacuum.

Metathetical Reactions. *cis*-Dibromo-*cis*-1,2-bis(diphenylphosphino)-3,3,3-trifluoroprop-1-enepalladium(II), $Br_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$. *cis*-$Cl_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$ (0.5 g) and KBr (2.5 g) were stirred together overnight in acetone (100 mL). The solvent was removed under vacuum and the resulting residue extracted with CH_2Cl_2 (150 mL). The extract was filtered, dried over anhydrous $MgSO_4$, and evaporated to dryness to give the crude product as a pale yellow solid. Recrystallization from hot benzonitrile (20 mL) gave the pure complex in the form of a pale yellow, microcrystalline powder.

***cis*-Diiodo-*cis*-1,2-bis(diphenylphosphino)-3,3,3-trifluoroprop-1-enepalladium(II), $I_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$.** *cis*-$Cl_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$ (0.8 g) and KI (3 g) were stirred together overnight in acetone (100 mL). The solvent was removed under vacuum and the residue extracted with $CHCl_3$ (150 mL). The extract was filtered, dried over anhydrous $MgSO_4$, and concentrated under vacuum to a volume of ca. 20 mL. On standing at −10 °C for 3 days this solution deposited the pure complex in the form of a microcrystalline, orange powder which was filtered off and dried at ca. 120 °C (0.1 Torr) for 24 h.

Ligand Displacement Reactions. Both reaction and workup were carried out under a nitrogen atmosphere and all solvents were thoroughly deoxygenated before use by refluxing for several hours in a stream of nitrogen.

***cis*-$Ph_2PCH{=}C(R)PPh_2$ (R = CF_3, Ph), *cis*-$Ph_2PCH{=}C(R)PEtPh$ (R = CF_3, Ph), and *cis*-$Ph_2PCH{=}C(R)P(C_2H_4CN)_2$ (R = CF_3, Ph, *t*-Bu).** The platinum chloride complex (ca. 1 g) and KCN (12 g) were refluxed together overnight in a mixture of benzene (250 mL) and distilled, degassed water (120 mL). After cooling to room temperature, the organic layer was separated, washed with water (3 × 100 mL), and dried over anhydrous Na_2SO_4. The desiccant was filtered off and washed with benzene (20 mL); then the filtrate and washings were evaporated to dryness under vacuum to give the free diphosphine. In this way the following compounds were obtained: (1) *cis*-$Ph_2PCH{=}C(Ph)PPh_2$, *cis*-$Ph_2PCH{=}C(CF_3)PEtPh$, *cis*-$Ph_2PCH{=}C(CF_3)P(C_2H_4CN)_2$, and *cis*-$Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2$, in the form of viscous, straw-colored oils which did not crystallize during several weeks standing at 25 °C; (2) *cis*-$Ph_2PCH{=}C(Ph)EtPh$ and *cis*-$Ph_2PCH{=}C(t\text{-}Bu)P(C_2H_4CN)_2$, as viscous, straw-colored oils which crystallized on prolonged standing at 25 °C; (3) *cis*-$Ph_2PCH{=}C(CF_3)PPh_2$, as an oil which crystallized on standing for 3 days at 25 °C and was subsequently recrystallized from hot EtOH (2 mL) to give well-formed, colorless crystals.

***cis*-$Ph_2PCH{=}C(t\text{-}Bu)PPhR'$ (R′ = Ph, Et).** When the reaction of *cis*-$Cl_2Pt(Ph_2PCH{=}C(t\text{-}Bu)PEtPh)$ with KCN was carried out in benzene–water as described above, larger amounts of a white solid were present in the reaction mixture after overnight reflux. This precipitate was filtered off and identified from its IR spectrum as *cis*-$(CN)_2Pt(Ph_2PCH{=}C(t\text{-}Bu)PEtPh)$. The cyanide complex (0.85 g) and KCN (8 g) were subsequently suspended in a mixture of water (100 mL) and acetone (75 mL) and the suspension was stirred and heated to reflux under nitrogen. Shortly after reaching reflux temperature, all of the solids dissolved to give a clear, colorless solution. Reflux was continued overnight and the nitrogen flow maintained at a brisk rate so that much of the acetone was blown off. This resulted in precipitation of the displaced diphosphine which, after cooling to 25 °C, was filtered off, washed with water (2 × 10 mL), and dried under vacuum to give pure *cis*-$Ph_2PCH{=}C(t\text{-}Bu)PEtPh$.

cis-$Ph_2PCH{=}C(t\text{-}Bu)PPh_2$ was similarly obtained from the reaction of *cis*-$(CN)_2Pt(Ph_2PCH{=}C(t\text{-}Bu)PPh_2)$ (0.47 g) and KCN (4 g) in acetone (40 mL) and water (60 mL).

Preparation of the Nickel(II) Complexes. *cis*-Dichloro-*cis*-α,β-bis(diphenylphosphino)styrenenickel(II), $Cl_2Ni(Ph_2PCH{=}C(Ph)PPh_2)$. A solution of *cis*-$Ph_2PCH{=}C(Ph)PPh_2$ (0.47 g, 1.0 mmol) in EtOH (5 mL) was added to a stirred suspension of finely ground anhydrous nickel(II) chloride (0.13 g, 1.0 mmol) in refluxing EtOH (35 mL). The resulting red reaction mixture was stirred at reflux for a further 2 h; then the orange-brown precipitate of the crude complex which formed during this time was filtered off and dried. Recrystallization from 1:1 CH_2Cl_2–EtOH gave red-brown crystals of the pure complex.

***cis*-Dichloro-*cis*-1,2-bis(diphenylphosphino)-3,3-dimethylbut-1-enenickel(II), $Cl_2Ni(Ph_2PCH{=}C(t\text{-}Bu)PPh_2)$.** A solution of *cis*-$Ph_2PCH{=}C(t\text{-}Bu)PPh_2$ (0.18 g, 0.4 mmol) in EtOH (10 mL) was added to a stirred suspension of fine-ground anhydrous nickel(II) chloride (0.052 g, 0.4 mmol) in refluxing EtOH (10 mL). The resulting red-colored reaction mixture was stirred at reflux for 2 h, then cooled and stirred at 25 °C for a further 1 h. The crude complex precipitated in the form of a golden yellow powder which was filtered off and dried. Recrystallization from 2:1 EtOH–CH_2Cl_2 afforded red-brown crystals of the pure complex.

***cis*-Dichloro-*cis*-1-diphenylphosphino-2-ethylphenylphosphino-3,3,3-trifluoroprop-1-enenickel(II), $Cl_2Ni(Ph_2PCH{=}C(CF_3)PEtPh)$.** This complex was prepared as for *cis*-$Cl_2Ni(Ph_2PCH{=}C(t\text{-}Bu)PPh_2)$, from *cis*-$Ph_2PCH{=}C(CF_3)PEtPh$ (0.20 g, 0.5 mmol) in EtOH (5 mL) and nickel(II) chloride (0.065 g, 0.5 mmol) in EtOH

(15 mL) and was recrystallized from 3:1 EtOH-CH_2Cl_2 to give red-brown rods.

***cis*-Dichloro-*cis*-α-bis(2-cyanoethyl)phosphino-β-diphenylphosphinostyrenenickel(II), $Cl_2Ni[Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2]$.** A solution of *cis*-$Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2$ (0.18 g, 0.4 mmol) in EtOH (5 mL) was added to a stirred suspension of finely ground anhydrous nickel(II) chloride (0.052 g, 0.4 mmol) in refluxing EtOH (15 mL). After stirring at reflux for 2.5 h all of the nickel chloride had dissolved to give a clear, orange-red solution which was concentrated to ca. 10 mL by allowing EtOH to boil off. On cooling to room temperature and subsequent storage at −10 °C for 3 days the complex was deposited as an orange-brown precipitate which was filtered off and dried under vacuum.

Results and Discussion

The 1:1 reaction of secondary phosphines $HPPh_2$, HPEtPh, and $HP(C_2H_4CN)_2$ with Pd(II) and Pt(II) complexes **1** (R = CF_3, Ph, *t*-Bu) proceeds readily in benzene at 25 °C or in CH_2Cl_2 at −78 °C to give the *cis*-1,2-diphosphinoalk-1-ene complexes (**3**) plus 1 mol of the corresponding phosphinoalkyne (eq 2). The diphosphine complexes exhibit a wide range of solubilities and the only major synthetic difficulties encountered lay in separating the more soluble members of the series from their reaction solutions, particularly in cases where the displaced phosphinoalkyne began to polymerize once no longer coordinated (e.g., $Ph_2PC{\equiv}CCF_3$). For the most part, however, the diphosphine complexes could be readily isolated in good yield, in contrast to analogous reactions employing dicyclohexylphosphine, which are much less clean. The mechanisms of these addition reactions, including those with dicyclohexylphosphine, will be discussed in detail elsewhere.[29] This synthetic route to olefinic diphosphine complexes is a very useful one, with potential applicability to many other systems where phosphorus coordinated phosphinoalkyne complexes are accessible. Few unsymmetrical olefinic diphosphine complexes are known, principally because more conventional routes to the free ligands are fraught with difficulty.[5,7]

In order to calculate ^{31}P coordination chemical shifts for the complexes it was necessary to measure ^{31}P NMR spectra of the free diphosphines. Consequently, small amounts of the free *cis*-1,2-diphosphinoalk-1-ene ligands were obtained for characterization purposes by displacement from the corresponding Pt(II) complex using excess KCN (eq 3).

$$\underset{\mathbf{3}}{Cl_2Pt(Ph_2PCH{=}C(R)PR'R'')}$$

$$\xrightarrow{CN^-} \underset{\mathbf{4}}{(CN)_2Pt(Ph_2PCH{=}C(R)PR'R'')}$$

$$\xrightarrow{CN^-} \underset{\mathbf{5}}{Ph_2PCH{=}C(R)PR'R''} + [Pt(CN)_4]^{2-} \quad \ldots. \quad (3)$$

The reaction was normally carried out in a benzene–water mixture and proceeded straightforwardly,[30,31] with the exception of two cases (R = *t*-Bu, R′ = R″ = Ph, and R = *t*-Bu, R′ = Et, R″ = Ph) in which the intermediate bis(cyano) complex **4** was so insoluble in this medium that it precipitated and did not react further. When transferred to an acetone–water mixture however, the precipitated complexes **4** could be reacted further with excess cyanide liberating the desired diphosphine. The free ligands were viscous, straw-colored oils or low-melting solids which were mostly stable toward aerial oxidation and/or polymerization for several weeks. As would be expected, the most sensitive of the ligands were those bearing terminal alkyl groups and having electron-withdrawing substituents on the backbone and it proved impossible to obtain samples of *cis*-$Ph_2PCH{=}C(R)P(C_2H_4CN)_2$ (R = Ph, CF_3) which were completely free from trace impurities. Mass spectra of these two ligands, however, showed no peaks assignable to phosphine oxide or bis(phosphine oxide) molecular ions, suggesting that the impurities present may have derived from polymerization rather than oxidative decomposition.

The nickel(II) complexes reported here were all obtained by direct reaction of the free diphosphine with anhydrous nickel(II) chloride, rather than by a secondary phosphine addition reaction of the type used to prepare the Pd(II) and Pt(II) analogues. This was a result of our inability thus far to obtain substrates $Cl_2Ni(Ph_2PC{\equiv}CR)_2$. The direct reactions were carried out as described[32] for the parent *cis*-$Ph_2PCH{=}CHPPh_2$.

Infrared data (Table II) have been deposited as supplementary information. For those complexes where R = CF_3 and for some of the free diphosphines, a band of medium intensity between 1580 and 1590 cm^{-1} could be assigned to $\nu_{C=C}$ of the diphosphinoalk-1-ene. In most of the complexes, however, and in all of the free diphosphines having R′ = R″ = C_2H_4CN, the $\nu_{C=C}$ vibration was too weak to be differentiated from the other weak bands which occur in the region 1550–1600 cm^{-1} for all aryl phosphines. The position of the $\nu_{C=C}$ band was insensitive both to coordination and to changes in M, X, R′, and R″. The observation of two ν_{M-Cl} modes in far-IR spectra of the complexes confirmed their cis configuration.

^1H NMR spectra (Table III) are included as supplementary data. Where R = *t*-Bu, Ph, spectra showed a doublet resonance in the region 6.4–6.75 ppm which may be assigned to the unique vinylic proton. In those complexes for which R = CF_3 (except M = Ni) and in all of the free diphosphines this resonance was obscured by the aromatic multiplet. Both the shift and the coupling constant of the vinyl proton resonance appear relatively invariant, except in the Ni(II) complexes, where the shift occurs at slightly higher field and the doublet separation is somewhat smaller than for Pd(II) and Pt(II). The doublet separation presumably must be written as $|^2J_{P-H} + {}^3J_{P-H}|$, although the existence of a significant contribution from $^3J_{P-H}$ is open to question. Unfortunately, there is little ^1H NMR data available for comparable vinylic phosphines and their complexes. In *cis*- and *trans*-$Ph_2PCH{=}CHR$ (R = Ph,[33] PPh_2[34]), the resonances due to the vinylic protons are partially obscured by the aromatics, but it is noteworthy that the vinylic protons in *trans*-$Ph_2PCH{=}CHPPh_2$ give rise to a triplet, $|J|$ = 15 Hz,[34] suggesting a nonzero $^3J_{P-H}$ in this case at least. Even less information exists concerning analogues of complexes **3**. Although complexes of VPP with Ni(II)[32] and Pd(II)[35] are known, their NMR spectra have not been reported. Other resonances in the ^1H NMR spectra of complexes **3** and ligands **5** are consistent with their formulation but otherwise uninformative. Ethyl and 2-cyanoethyl groups present in these species gave second-order spectra in the form of broad, unresolved multiplets and no attempt was made to analyze these.

^{31}P NMR data appear in Table IV. Of the free diphosphines, only those for which R = *t*-Bu give first-order AX spectra whereas those where R = CF_3 and Ph exhibit AB spectra. In two of the latter cases [*cis*-$Ph_2PCH{=}C(CF_3)PEtPh$ and *cis*-$Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2$] the intense inner two lines of the AB pattern coalesce and the weak outer lines become too weak to be observed, with the result that a deceptively simple single-line spectrum is obtained (i.e., effectively A_2 under the spectrometer conditions). No coupling constant information may be extracted from such spectra and the observed chemical shift of the singlet is an average value of the true shifts of the two phosphorus atoms. Such single-line spectra are only obtained when the ratio of the chemical shift difference between the two phosphorus atoms (δ_L) to the coupling constant between them ($|^3J_{P-P}|$ in this case) becomes very small ($\delta_L/J \leq$ ca. 1).[36] If it is assumed that $|^3J_{P-P}|$ in the diphosphines having singlet spectra is of the same order of magnitude as those of the other ligands with R = CF_3 and Ph (i.e., ca. 150 Hz), then δ_L is unlikely to exceed ca. 150 Hz (i.e.,

Table I. Preparative Data for Diphosphines $Ph_2PCH{=}C(R)PR'R''$ and Their Complexes with Ni(II), Pd(II), and Pt(II)

	Yield,[a]		% C		% H		% P		% halogen		% N		mol[b]
	%	mp, °C	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found	wt
cis-$Ph_2PCH{=}C(CF_3)PPh_2$	55	72–74	69.83	70.07	4.56	4.58	13.34	13.46					464 (61)
cis-$Ph_2PCH{=}C(Ph)PPh_2$	88	oil	81.34	81.23	5.55	5.75	13.11	13.04					473 (8)
cis-$Ph_2PCH{=}C(t\text{-}Bu)PPh_2$	77	93–95	79.63	78.74	6.68	6.70	13.69	13.21					453 (9)
cis-$Ph_2PCH{=}C(CF_3)PEtPh$	70	oil	66.35	66.17	5.08	4.99	14.88	14.67					416 (20)
cis-$Ph_2PCH{=}C(Ph)PEtPh$	92	108–110	79.23	79.13	6.17	6.36	14.59	14.54					424 (31)
cis-$Ph_2PCH{=}C(t\text{-}Bu)PEtPh$	61	97–101	77.21	77.05	7.48	7.47	15.32	15.23					404 (50)
cis-$Ph_2PCH{=}C(CF_3)P(C_2H_4CN)_2$	44	oil	60.29	58.48	4.58	5.17	14.81	15.76			6.70	10.11	418 (30)
cis-$Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2$	83	oil	73.23	74.20	5.67	5.84	14.53	13.81			6.57	5.80	426 (16)
cis-$Ph_2PCH{=}C(t\text{-}Bu)P(C_2H_4CN)_2$	90	77–82	70.92	71.02	6.94	7.03	15.24	15.29			6.89	6.65	406 (1)
$Cl_2Ni(Ph_2PCH{=}C(Ph)PPh_2)$	53	350–370 dec	63.83	63.70	4.35	4.17	10.29	10.40	11.78	12.05			
$Cl_2Ni(Ph_2PCH{=}C(t\text{-}Bu)PPh_2)$	49	335–350 dec	61.90	61.87	5.19	5.30	10.64	10.77	12.18	12.21			
$Cl_2Ni(Ph_2PCH{=}C(CF_3)PEtPh)$	50	290–295 dec	50.59	50.71	3.88	3.76	11.35	11.47	12.99	13.09			
$Cl_2Ni[Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2]$	18	260–265 dec	56.16	54.62	4.35	4.44							
$Cl_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$	61	dec >275	50.53	50.63	3.31	3.40	9.65	9.60	11.05	11.25			
$Br_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$	40	dec >330	44.39	44.50	2.90	2.90	8.48	8.53	21.87	21.61			
$I_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$	32	350–360 dec	39.33	39.16	2.57	2.63	7.51	7.54					
$Cl_2Pd(Ph_2PCH{=}C(Ph)PPh_2)$	52	dec >300	59.15	59.35	4.03	4.15	9.53	9.67	10.91	11.10			
$Cl_2Pd(Ph_2PCH{=}C(Ph)PEtPh)$	45	dec >225	55.89	55.70	4.36	4.32	10.29	10.37	11.78	11.99			
$Cl_2Pd[Ph_2PCH{=}C(CF_3)P(C_2H_4CN)_2]$	27	245–255 dec	42.32	42.30	3.21	3.35	10.40	10.17	11.93	12.03	4.70	4.44	
$Cl_2Pd[Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2]$	80	dec >120	51.73	51.90	4.01	4.02	10.26	10.42	11.74	11.59	4.64	4.49	604 (615)
$Cl_2Pt(Ph_2PCH{=}C(CF_3)PPh_2)$	69	>360	44.39	44.16	2.90	3.04	8.48	8.20	9.70	9.78			
$Cl_2Pt(Ph_2PCH{=}C(Ph)PPh_2)$	86	>360	52.04	51.90	3.55	3.68	8.39	8.18	9.60	11.47			
$Cl_2Pt(Ph_2PCH{=}C(t\text{-}Bu)PPh_2)$	85	>360	50.15	49.97	4.21	4.21	8.62	8.68	9.87	10.02			
$Cl_2Pt(Ph_2PCH{=}C(CF_3)PEtPh)$	31	310–315 dec	40.48	40.26	3.10	3.15	9.08	9.32	10.39	10.38			
$Cl_2Pt(Ph_2PCH{=}C(Ph)PEtPh)$	68	325–330 dec	48.71	48.86	3.80	3.88	8.97	8.77	10.27	10.49			690 (677)
$Cl_2Pt(Ph_2PCH{=}C(t\text{-}Bu)PEtPh)$	31	328–332 dec	46.58	46.48	4.51	4.43	9.24	9.37	10.58	10.60			
$Cl_2Pt[Ph_2PCH{=}C(t\text{-}Bu)P(C_2H_4CN)_2]$	82	220–230 dec	42.87	42.68	4.20	4.26	9.21	9.50	10.55	10.41	4.17	4.35	

[a] Yields of the diphosphines are based on $Cl_2Pt(Ph_2PCH{=}C(R)PR'R'')$, those of the nickel complexes on $Ph_2PCH{=}C(R)PR'R''$, those of the Pd(II) and Pt(II) chloride complexes on $Cl_2M(Ph_2PC{\equiv}CR)_2$, and those of the Pd(II) bromide and iodide on $Cl_2Pd(Ph_2PCH{=}C(CF_3)PPh_2)$. [b] *m/e* (rel intensity) for the molecular ions of the diphosphines and molecular weight calculated (found) for the complexes in $CHCl_3$.

ca. 6 ppm). Thus, although only the average chemical shift is known for such ligands, the true shifts should lie within ca. 3 ppm of this value. This uncertainty in the true chemical shifts for the free diphosphines is sufficiently small when compared to the coordination chemical shifts observed (see Table IV and the discussion below) that the error involved in calculating the coordination chemical shift from the average ligand shift is small in these cases.

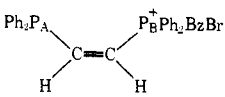
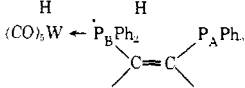
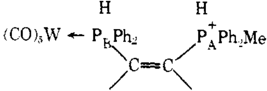
The predominant factor affecting ^{31}P NMR spectra of the uncoordinated diphosphines appears to be the nature of R rather than that of the terminal groups R′ and R″. Chemical shifts of the $Ph_2PCH{=}$ end of the ligands lie between ca. −23 and −36 ppm and have similar values for a given R. These shifts are in good agreement with existing values for uncoordinated $Ph_2PCH{=}$ in *cis*-1,2-diphosphinoalk-1-enes (Table V). The assignment of resonances was also confirmed by selective ^1H decoupling[9] of the ^{31}P NMR spectrum for *cis*-$Ph_2PCH{=}C(t\text{-}Bu)P(C_2H_4CN)_2$. Irradiation only in the frequency range for aliphatic protons gave a spectrum in which the resonance at −35.5 ppm was broadened while that at −25.0

Table IV. ^{31}P NMR Data for Diphosphines *cis*-Ph$_2$PCH=C(R)PR′R″ and Their Complexes with Ni(II), Pd(II), and Pt(II)^{d}

	PPh$_2$				PR′R″				
	δ	Δ_{obsd}	Δ_R	$^1J_{^{195}Pt-^{31}P}$	δ	Δ_{obsd}	Δ_R	$^1J_{^{195}Pt-^{31}P}$	$\lvert J_{P-P}\rvert$
cis-Ph$_2$PCH=C(CF$_3$)PPh$_2$	−26.3				−18.0				131
cis-Ph$_2$PCH=C(Ph)PPh$_2$	−28.1				−7.0				146
cis-Ph$_2$PCH=C(*t*-Bu)PPh$_2$	−32.2				−14.8				37
cis-Ph$_2$PCH=C(CF$_3$)PEtPh	−25.8^{a}				−25.8^{a}				*a*
cis-Ph$_2$PCH=C(Ph)PEtPh	−27.8				−21.1				146
cis-Ph$_2$PCH=C(*t*-Bu)PEtPh	−32.5				−15.8				45
cis-Ph$_2$PCH=C(CF$_3$)P(C$_2$H$_4$CN)$_2$	−23.0				−32.9				131
cis-Ph$_2$PCH=C(Ph)P(C$_2$H$_4$CN)$_2$	−28.2^{a}				−28.2^{a}				*a*
cis-Ph$_2$PCH=C(*t*-Bu)P(C$_2$H$_4$CN)$_2$	−35.5				−25.0				18
Cl$_2$Ni(Ph$_2$PCH=C(Ph)PPh$_2$)	46.0	74.1	43.4		69.3	76.3	53.2		69
Cl$_2$Ni(Ph$_2$PCH=C(*t*-Bu)PPh$_2$)	43.8	76.0	44.0		72.1	86.9	60.6		71
Cl$_2$Ni(Ph$_2$PCH=C(CF$_3$)PEtPh)	48.0	73.8	43.9		69.9	95.7	65.8		66
Cl$_2$Ni[Ph$_2$PCH=C(Ph)P(C$_2$H$_4$CN)$_2$]	48.1	76.4	45.6		74.3	102.5	71.8		63
Cl$_2$Pd(Ph$_2$PCH=C(CF$_3$)PPh$_2$)	56.6	82.9	36.5		73.6	91.6	47.8		21
Br$_2$Pd(Ph$_2$PCH=C(CF$_3$)PPh$_2$)	56.0	82.3	*d*		73.5	91.5	*d*		27
I$_2$Pd(Ph$_2$PCH=C(CF$_3$)PPh$_2$)	47.6	73.9	*d*		67.6	85.6	*d*		22
Cl$_2$Pd(Ph$_2$PCH=C(Ph)PPh$_2$)	51.1	79.2	32.2		75.6	82.6	42.3		15
Cl$_2$Pd(Ph$_2$PCH=C(Ph)PEtPh)	51.4	79.2	32.3		80.4	102.2	57.4		17
Cl$_2$Pd[Ph$_2$PCH=C(CF$_3$)P(C$_2$H$_4$CN)$_2$]	54.6	77.6	32.3		77.1	110.0	61.5		20
Cl$_2$Pd[Ph$_2$PCH=C(Ph)P(C$_2$H$_4$CN)$_2$]	53.6	81.8^{b}	34.8^{b}		81.7	109.9^{b}	62.9^{b}		13
Cl$_2$Pt(Ph$_2$PCH=C(CF$_3$)PPh$_2$)	31.8	58.1	30.7	*c*	48.3	66.3	41.6	*c*	<2
Cl$_2$Pt(Ph$_2$PCH=C(Ph)PPh$_2$)	30.5	58.6	30.6	3552	53.1	60.1	39.0	3640	<2
Cl$_2$Pt(Ph$_2$PCH=C(*t*-Bu)PPh$_2$)	25.9	58.1	28.8	3425	53.2	68.0	44.3	3613	<2
Cl$_2$Pt(Ph$_2$PCH=C(CF$_3$)PEtPh)	31.9	57.7^{b}	30.5^{b}	3648	54.3	80.1^{b}	52.9^{b}	3652	<2
Cl$_2$Pt(Ph$_2$PCH=C(Ph)PEtPh)	30.4	58.2	30.3	3640	55.5	76.6	50.9	3554	<2
Cl$_2$Pt(Ph$_2$PCH=C(*t*-Bu)PEtPh)	26.7	59.2	29.8	3606	60.9	76.7	52.7	3531	<2
Cl$_2$Pt[Ph$_2$PCH=C(*t*-Bu)P(C$_2$H$_4$CN)$_2$]	26.4	61.9	31.5	3530	64.5	89.5	62.5	3474	<2

[a] A$_2$ spectrum δ is an average value and no J_{P-P} observed. [b] Calculated from the average shift observed in the A$_2$ spectrum of the free ligand. [c] The complex was too insoluble and the solution too weak to observe the $^1J_{^{195}Pt-^{31}P}$ satellites. [d] In CDCl$_3$.

Table V. Literature ^{31}P NMR Data for *cis*-1,2-Diphosphinoalk-1-enes[39]

	δ_{P_A}^{a}	δ_{P_B}^{a}	$\lvert ^3J_{P_A-P_B}\rvert$^{b}
	−24.75	+13.81	18.7
	−28.68	+4.90	37.2
	+10.43	+11.69	11.2

[a] In parts per million with respect to 85% H$_3$PO$_4$. Positive shifts are to low field. [b] In hertz.

Table VI. Literature Values of $\lvert ^2J_{PMP}\rvert$^{a} in Complexes *cis*-X$_2$ML$_2$

	Ni	Pd	Pt	ref
Cl$_2$M(PMe$_3$)$_2$		8.0	18.9	38
Br$_2$M(PMe$_3$)$_2$		1.0	16.2	38
Cl$_2$M(HP-*t*-Bu$_2$)$_2$	2	2	0	40
Br$_2$M(HP-*t*-Bu$_2$)$_2$	5	5	0	40
Cl$_2$M(P(OMe)$_3$)$_2$		77.9	17.8	38
Cl$_2$M(Me$_2$PCH$_2$CH$_2$PPh$_2$)	76	10	<2	22

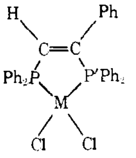
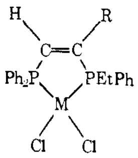
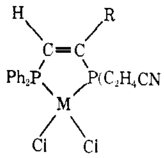
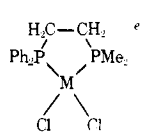
[a] In hertz.

ppm remained sharp and well resolved. Irradiation of only aromatic protons had the reverse effect, broadening the signal at −25.0 ppm whereas the high-field resonance reverted to a well-resolved doublet.

For R = *t*-Bu, $\lvert ^3J_{P-P}\rvert$ values fall within the range 18–45 Hz, somewhat larger than the couplings of 25–30 Hz observed in saturated analogues Ph$_2$PCH$_2$CH$_2$PPhR (R = alkyl),[9] Ph$_2$PCH$_2$CH$_2$P-*n*-Bu$_2$,[10] and Ph$_2$PCH$_2$CH$_2$PMe$_2$[22] and in reasonable agreement with the limited data available for such couplings within *cis*-1,2-diphosphinoalk-1-ene systems (Table V). For R = CF$_3$ and Ph, however, $\lvert ^3J_{P-P}\rvert$ values, where measurable, become surprisingly large, although still dependent upon R (R = CF$_3$, $\lvert ^3J_{PP}\rvert$ = 131 Hz; R = Ph, $\lvert ^3J_{PP}\rvert$ = 146 Hz). Presumably the larger values reflect the greater electron-withdrawing power of these substituents compared to the *t*-Bu group, but the observation of larger couplings for R = Ph than for R = CF$_3$ would also suggest that electronegativity is not the only pertinent factor. Conjugation of the phenyl substituent with the alkene double bond and the resulting coplanarity of the entire ligand skeleton are factors which may be of importance. However, the range of systems examined to date, further limited by the A$_2$ spectra sometimes obtained, remains too small to confirm such hypotheses.

In contrast to P–P couplings within the free diphosphines, the couplings observed in their complexes **3** are relatively unaffected by changes in R, but rather are determined by the nature of M. Although there has been considerable attention devoted in recent years[24,38] to the measurement and elucidation of P–P couplings transmitted through a metal center ($^2J_{PMP}$), the variation of $^2J_{PMP}$ within complexes of the type *cis*-X$_2$ML$_2$ (M = Ni, Pd, Pt) is by no means clearly established. Most couplings obtained to date have been measured indirectly from the ^{19}F or ^{1}H NMR spectra of complexes where L is a fluorophosphine or a phosphine bearing methyl or methoxy substituents. Such measurements have established that $^2J_{P-P}$ is generally much larger in trans complexes than in their cis isomers and that $^2J_{PMP}$ for cis complexes is almost invariably negative.[37,38] The series of related Pd(II) and Pt(II) complexes used in these measurements has, however, rarely been extended to include Ni(*II*) (in part a result of synthetic difficulties) and the results obtained for Pd(II) and Pt(II) are often conflicting as to the effect on $^2J_{PMP}$ of varying the metal atom (Table VI). Our results agree well with the single set of values previously reported for the analogous saturated complexes *cis*-

Table VII. Variation of Δ_R[a] within Saturated and Unsaturated Five-Membered Rings

							 [e]	
	PPh_2	$P'Ph_2$	PPh_2	PEtPh	PPh_2	$P(C_2H_4CN)_2$	PPh_2	PMe_2
Ni	43.4	53.2	43.9[b]	65.8[b]	45.6[c]	71.8[c]	46.1	59.6
Pd	32.2	42.3	32.3[c]	57.4[c]	34.8[c]	62.9[c]	35.6	53.8
Pt	30.6	39.0	30.5[b]	52.9[b]	31.5[d]	62.5[d]	32.5	44.6
			30.3[c]	50.9[c]				

[a] In parts per million. A positive Δ_R is a deshielding contribution. [b] R = CF_3. [c] R = Ph. [d] R = *t*-Bu. [e] Values calculated from ref 21.

$Cl_2M(Ph_2PCH_2CH_2PMe_2)$ (Table VI) and are also consistent with the order which is now well established[13,22,24] for the series *cis*-$L_2M(CO)_4$ (M = Cr, Mo, W), i.e., the magnitude of $^2J_{PMP}$ decreases going down the group. Otherwise, P–P couplings for the complexes **3** remain relatively constant for a given metal atom, variations due to changes in X, R, R′, and R″ being relatively small and conforming to no obvious pattern.

In chelate rings of the type present in **3**, the observed P–P coupling constant $|J_{PP}{}^{obsd}|$ might be expected to include contributions due to transmission both through the ligand backbone ($J_{PP}{}^B$) and through the metal atom ($^2J_{PMP}$), i.e., $|J_{PP}{}^{obsd}| = |J_{PP}{}^B + {}^2J_{PMP}|$. Such an effect was first described for the series *cis*-$[EtN(PF_2)_2]M(CO)_4$ (M = Cr, Mo, W)[24] and it was observed that $J_{PP}{}^B$ was positive whereas $^2J_{PMP}$ had a negative sign. Similarly, this effect was more recently invoked to explain the coupling constants observed for complexes *cis*-(L-L′)M(CO)$_4$ (M = Cr, Mo, W; L-L′ = $Ph_2P(CH_2)_n$-$OPPh_2$, *n* = 1, 2;[13] $Ph_2P(CH_2)_nPR'R''$, *n* = 1, 2, 3;[12] $Ph_2PCH_2CH_2PMe_2$[22]), $J_{PP}{}^B$ being assumed to have the same magnitude as $|^3J_{PP}|$ in the free diphosphine or in a bimetallic diphosphine-bridged analogue and the signs of $^2J_{PMP}$ and $J_{PP}{}^B$ again being assumed opposite.

An analysis of our data for the range of complexes of type **3** brings out the following points: (a) Values of $|J_{PP}{}^{obsd}|$ for a given metal are closely similar and show no marked variation with group R on the ligand backbone. Thus for *cis*-$Cl_2Ni(Ph_2PCH{=}C(R)PPh_2)$ $|J_{PP}{}^{obsd}|$ differs by only 2 Hz for R = Ph and R = *t*-Bu. This is in sharp contrast to the difference of 109 Hz in $^3J_{PP}$ for the free ligands. (b) The absolute magnitudes of $J_{PP}{}^{obsd}$ for the nickel, palladium, and platinum complexes of type **3** with the ligand skeleton $>PCH{=}C(R)$-$P<$ closely resemble values for the diphosphine series *cis*-$Cl_2M(Ph_2PCH_2CH_2PMe_2)$ having a saturated ligand backbone.[22] (c) The values of $|J_{PP}{}^{obsd}|$ (0–27 Hz) for the palladium and platinum derivatives are in the range normally found (Table VI) for J_{PP} in cis phosphine complexes[24,38] where the two phosphorus atoms are not connected by a ligand backbone. It is not impossible that observation (a) could be accounted for by a combination of coupling constants of different signs and magnitudes. Thus hypothetically a $J_{PP}{}^{obsd}$ of −71 Hz in $Cl_2Ni(Ph_2PCH{=}C(t\text{-}Bu)PPh_2)$ could result from a $^2J_{PNiP}$ of −34 Hz and a $J_{PP}{}^B$ of −37 Hz identical with that in the ligand while $J_{PP}{}^{obsd}$ of −69 Hz in $Cl_2Ni(Ph_2PCH{=}C(Ph)$-$PPh_2)$ could result from $^2J_{PNiP}$ of +77 Hz and $J_{PP}{}^B$ of −146 Hz (as in $Ph_2PCH{=}C(Ph)PPh_2$). It would be remarkable, however, if a group R on the ligand backbone, remote from the metal, could effect sign and magnitude changes for J_{PMP} in this way. A more likely explanation is that any contributions of $J_{PP}{}^B$ to the observed couplings, if they exist at all, are much smaller than $|^3J_{PP}|$ in the free diphosphines. Further evidence to support this argument comes from the platinum series where, in order to account for $|J_{PP}{}^{obsd}|$ values of <2 Hz, $^2J_{PMP}$ values well outside the normal range of cis P–P couplings in Pd(II) and Pt(II) complexes[24,38] would need to be postulated if backbone contributions to $|J_{PP}{}^{obsd}|$ were of the same magnitude as in the free ligands. Observation (b) is significant, since, if taken at its face value, it implies that neither a change in the degree of unsaturation in the ligand skeleton nor a change in substituents on the backbone has much effect on $|J_{PP}{}^{obsd}|$.

The simplest rationale for all of the facts alluded to above and one which we favor is that it is unnecessary to assume major contributions from backbone coupling to $|J_{PP}{}^{obsd}|$ in complexes of type **3**. This hypothesis thus suggests that a fundamental change in coupling through the metal atom is responsible for the observed decrease in $|J_{PP}{}^{obsd}|$ down the series Ni > Pd > Pt. Furthermore, in view of the close similarities between $|J_{PP}{}^{obsd}|$ for complexes **3** and the corresponding $Ph_2PCH_2CH_2PMe_2$-containing derivatives,[22] we doubt that $J_{PP}{}^B$ contributions can be responsible for the decrease in $|J_{PP}{}^{obsd}|$ down the nickel group series *cis*-$Cl_2M(Ph_2PCH_2CH_2PPh_2)$ (M = Ni, Pd, Pt).

It is interesting to speculate why the strong $|^3J_{PP}|$ couplings present in the free diphosphines **5** when R = CF_3 and Ph might be greatly reduced in their complexes **3**. Since it has been noted in the past that such couplings are highly dependent on dihedral angles,[39] the most likely explanation would seem to be that distortions of the ligand skeleton and ring strain, perhaps with loss of planarity, on complexation greatly reduce the effectiveness of transmission through the olefinic linkage. A single-crystal X-ray analysis of *cis*-$Cl_2Ni(Ph_2PCH{=}C(Ph)$-$PPh_2)$ has revealed that the olefinic carbon atom bearing the phenyl substituent lies ~0.1 Å out of the plane defined by the nickel, two chlorine, two phosphorus, and second olefinic carbon atom.[42] Moreover, the phenyl substituent is tilted markedly out of this plane owing to unfavorable steric interactions with the diphenylphosphido group.

It has been noted recently[13,22,26] that phosphorus atoms present in five-membered chelate rings exhibit anomalously large coordination chemical shifts (Δ). Such values are "anomalous" in the sense that they are much larger than the coordination shifts in nonchelated analogues and cannot be predicted from the linear relationship between the chemical shift of the free phosphine (δ_F) and the coordination chemical shift (i.e., $\Delta = A\delta_F + B$) which has been shown[43] to hold for a variety of transition-metal complexes. To facilitate discussion of this effect it is thus convenient to regard the observed coordination chemical shift in such rings (Δ_{obsd}) as being made up of a "normal" coordination shift Δ_N (predicted from the $\Delta = A\delta_F + B$ relationship or measured for a nonchelated analogue) and a "ring contribution" Δ_R,[26] i.e., $\Delta_{obsd} = \Delta_N + \Delta_R$. It must be stressed that the accuracy and reliability of the Δ_R values discussed here must of necessity reflect the accuracy with which Δ_N may be determined. Also, an additional inaccuracy in the determination of Δ_{obsd} itself is introduced for those cases in which the free diphosphines give A_2 spectra (vide supra). The Δ_R data appearing in Tables IV and VII were in all cases based on Δ_N values derived from the $\Delta = A\delta_F + B$ relationship. Values of A and B have been published[43] for tertiary phosphine complexes *cis*-Cl_2ML_2 where M = Pd ($A = -0.315, B = -38.11$) and Pt ($A = -0.326, B = -18{,}83$) but not for M = Ni. Employing the literature values[44] for ten complexes of the type *cis*-$Cl_2Ni(PR_3)_2$ (R = alkyl) we have derived values of $A = -0.330$ and $B = -21.43$ for this series. In view of the inaccuracies involved in predicting Δ_N values on this basis (particularly in the nickel series) no great significance should be attached to any one individual Δ_R value presented here. Taken as a whole, however, we feel that the observed differences in Δ_R illustrated in Table VII are both too large and too consistent to be purely the spurious result of inaccuracies in the determination of Δ_{obsd} and Δ_N.

Values of the chemical shift, Δ_{obsd}, and Δ_R appear in Table IV and correlations of Δ_R with changes in molecular structure appear in Table VII. The assignment of resonances in the complexes was confirmed by selective ^1H decoupling of the ^{31}P NMR spectra of *cis*-$Cl_2Pd[Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2]$ and *cis*-$Cl_2Pt[Ph_2PCH{=}C(t\text{-}Bu)P(C_2H_4CN)_2]$, as described earlier for free $Ph_2PCH{=}C(t\text{-}Bu)P(C_2H_4CN)_2$. The $Ph_2PCH{=}$ ends of the coordinated diphosphines have very similar chemical shifts for a given metal atom and give Δ_{obsd} and Δ_R values which vary within a remarkably narrow range given the uncertainties in their determination which were discussed earlier (Table IV). Furthermore, this similarity in Δ_R values for the PPh_2 position in five-membered rings extends to the saturated analogues *cis*-$Cl_2M(Ph_2PCH_2CH_2PMe_2)$ (Table VII), suggesting that Δ_R is unaffected by any of the steric and electronic differences involved in the formation of saturated rings as opposed to unsaturated rings. Δ_R values for the PR′R″ position in complexes **3** consistently increase as the number of alkyl substituents increases. Typical increases in Δ_R amount to ca. 40–50% on going from R′ = R″ = Ph to R′ = R″ = C_2H_4CN and are observed for all metals. Similarly Δ_R for the PMe_2 position is in all cases greater than that for the PPh_2 position in the saturated rings (Table VII). For both ends of the diphosphines and for both saturated and unsaturated five-membered chelates, Δ_R increases in the order Pt < Pd ≪ Ni.

Although these correlations of Δ_R with structure may prove empirically useful, they unfortunately contribute little toward an understanding of the origin of such ring contributions. It is known that deshielding ring contributions occur in a wide range of five-membered chelate complexes and for a variety of transition-metal ions and oxidation states, including not only diphosphines but also rings formed by ortho metalation and the "5.5-membered" rings present in 4-phosphinoalk-1-ene complexes.[26] The limited data available for ^{14}N coordination chemical shifts in complexes $[Co(NH_3)_6]^{3+}$,[45] $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$,[46] and $[Co(bpy)_3]^{3+}$ [45] suggests that a similar deshielding ring contribution may even occur in five-membered diamine rings. And yet, since it has been established that the effect is not directly related to bond-angle distortions arising from ring strain,[13] the origin of this widespread phenomenon presently remains obscure.

Acknowledgment. This work was supported by the National Research Council of Canada.

Supplementary Material Available: Table II, a compilation of infrared data for diphosphines and complexes, and Table III, a compilation of ^1H NMR spectral data (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Y. S. Wong, S. E. Jacobson, P. C. Chieh, and A. J. Carty, *Inorg. Chem.*, **13**, 284 (1974).

(2) A. J. Carty, S. E. Jacobson, R. T. Simpson, and N. J. Taylor, *J. Am. Chem. Soc.*, **97**, 7254 (1975).

(3) N. J. Taylor, S. E. Jacobson, and A. J. Carty, *Inorg. Chem.*, **14**, 2648 (1975).

(4) R. T. Simpson, S. E. Jacobson, A. J. Carty, M. Mathew, and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 388 (1973).

(5) R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, **91**, 5191 (1969).

(6) K. K. Chow, W. Levason, and C. A. McAuliffe, *Inorg. Chim. Acta*, **7**, 589 (1973).

(7) For a discussion of the difficulties encountered in carrying out stepwise reactions of *cis*-1,2-dichloroalk-1-enes with organophosphides see: K. K. Chow, W. Levason, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1429 (1976).

(8) Rigid chelating diphosphines are used extensively in transition metal catalyst systems for asymmetric synthesis. This has spurred a major effort to explore new synthetic routes to appropriately functionalized diphosphines and to elucidate pertinent aspects of their coordination chemistry. See, for example, (a) H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972); (b) K. Achiwa, *ibid.*, **98**, 8265 (1976); (c) M. E. Wilson, R. G. Nuzzo, and G. M. Whitesides, *ibid.*, **100**, 2269 (1978); (d) P. M. Treichel, W. L. Wong, and J. C. Calabrese, *J. Organomet. Chem.*, **159**, C20 (1978); (e) S. Brunie, J. Mazan, N. Langlois, and H. B. Kagan, *ibid.*, **114**, 225 (1976); (f) J. M. Brown and P. A. Chaloner, *J. Chem. Soc., Chem. Commun.*, 321 (1978); (g) A. R. Sanger and K. G. Tan, *Inorg. Chim. Acta*, **31**, L439 (1978).

(9) S. O. Grim, J. Del Gaudio, R. P. Molenda, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 3416 (1974).

(10) S. O. Grim and R. C. Barth, *J. Organomet. Chem.*, **94**, 327 (1975).

(11) S. O. Grim and J. D. Mitchell, *Inorg. Chem.*, **16**, 1770 (1977).

(12) S. O. Grim, R. C. Barth, J. D. Mitchell, and J. Del Gaudio, *Inorg. Chem.*, **16**, 1776 (1977).

(13) S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, **13**, 1095 (1974).

(14) S. O. Grim and J. D. Mitchell, *Synth. React. Inorg. Met.-Org. Chem.*, **4**, 221 (1974).

(15) S. O. Grim, L. C. Satek, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, **14**, 656 (1975).

(16) S. O. Grim and J. D. Mitchell, *Inorg. Chem.*, **16**, 1762 (1977).

(17) R. B. King, J. C. Cloyd, Jr., and R. H. Reimann, *J. Org. Chem.*, **41**, 972 (1976).

(18) R. B. King, J. C. Cloyd, Jr., and P. K. Hendrick, *J. Am. Chem. Soc.*, **95**, 5083 (1973).

(19) R. B. King and J. C. Cloyd, Jr., *J. Am. Chem. Soc.*, **97**, 46 (1975).

(20) R. B. King, J. C. Cloyd, Jr., and P. N. Kapoor, *J. Chem. Soc., Perkin Trans. 1*, 2226 (1973).

(21) R. B. King and J. C. Cloyd, Jr., *J. Am. Chem. Soc.*, **97**, 53 (1975).

(22) (a) R. B. King and J. C. Cloyd, Jr., *Inorg. Chem.*, **14**, 1550 (1975); (b) R. B. King, J. A. Zinich, and J. C. Cloyd, Jr., *ibid.*, **14**, 1554 (1975).

(23) (a) L. Manojlovic-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, W. E. Hill, J. V. Quagliano, and L. M. Vallarino, *J. Chem. Soc., Chem. Commun.*, 999 (1974); (b) L. D. Brown, S. Datta, J. K. Kouba, L. K. Smith, and S. S. Wreford, *Inorg. Chem.*, **17**, 729 (1978).

(24) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969).

(25) R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 (1969).

(26) P. E. Garrou, *Inorg. Chem.*, **14**, 1435 (1975).

(27) R. T. Simpson and A. J. Carty, *J. Coord. Chem.*, **2**, 207 (1973).

(28) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **2**, 306 (1963).

(29) A. J. Carty and D. K. Johnson, to be published.

(30) L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, **5**, 2212 (1966).

(31) B. Bosnich and S. B. Wild, *J. Am. Chem. Soc.*, **92**, 459 (1970).

(32) C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, **8**, 904 (1969).

(33) A. M. Aguiar and T. G. Archibald, *Tetrahedron Lett.*, **45**, 5471 (1966).

(34) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

(35) K. K. Chow, W. Levason, and C. A. McAuliffe, *Inorg. Chim. Acta*, **15**, 79 (1974).

(36) R. J. Abraham, "The Analysis of High Resolution NMR Spectra", Elsevier, Amsterdam, 1971, p 46.

(37) J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).

(38) R. J. Goodfellow and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1676 (1974).

(39) R. C. Taylor, R. L. Keiter, and L. W. Cary, *Inorg. Chem.*, **13**, 1928 (1974).

(40) A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Steinbank, *J. Chem. Soc. A*, 1826 (1971).

(41) R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 1908 (1970).

(42) G. Ferguson, personal communication.

(43) B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Steinbank, *Inorg. Nucl. Chem. Lett.*, **7**, 881 (1971).

(44) E. Fluck and J. Lorenz, *Z. Naturforsch. B*, **22**, 1095 (1967).

(45) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **8**, 19 (1964).

(46) B. M. Fung and S. C. Wei, *J. Magn. Reson.*, **3**, 1 (1970).