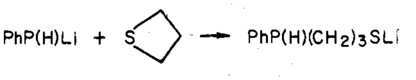
$$2PhP(Li)(CH_2)_3NH_2 + Br(CH_2)_3Br \rightarrow H_2N(CH_2)_3(Ph)P(CH_2)_3P(Ph)(CH_2)_3NH_2 + 2LiBr \quad (7)$$

ligand containing the S_2P_2 donor sets is an example of the versatility of the coupling method. Nucleophilic attack on trimethylene sulfide by lithium phenylphosphide produces an intermediate which can be easily coupled to form the S_2P_2 donor set (eq 8 and 9). Proton NMR studies have previously



(8)

$$2PhP(H)(CH_2)_3SLi + Br(CH_2)_3Br \rightarrow PhP(H)(CH_2)_3S(CH_2)_3S(CH_2)_3P(H)Ph + 2LiBr \quad (9)$$

shown that the S–H bond is is the most acidic bond in $PhHPCH_2CH_2CH_2SH$;[18] therefore, the mercaptide end functions as the nucleophile and the secondary phosphine assumes the terminal position in the coupling reaction.

Registry No. $Ph_2PCH_2CH_2CH_2Cl$, 57137-55-0; $Cy_2PCH_2CH_2CH_2Cl$, 71734-57-1; $Cy_2P(O)CH_2CH_2CH_2Cl$, 71734-58-2; PPH, 57322-05-1; $Ph_2P(O)CH_2CH_2CH_2PPh(O)OH$, 71734-59-3; PN_2, 6775-01-5; PHN, 13822-50-9; $Ph_2PCH_2CH_2Si(OEt)_3$, 18586-39-5; PS_2N_2, 71734-60-6; etp-CN, 71734-61-7; PP_2N, 71734-62-8; PPN, 71734-63-9; PPO, 71734-64-0; $PPNH_2$, 71734-65-1; P_2N_2, 71734-66-2; S_2P_2, 71734-67-3; Cy-ttp, 70786-89-9; $PhP(O)(CH_2CH_2CH_2P(O)Cy_2)_2$, 71734-68-4; ttp, 34989-06-5; Ph_2PLi, 4541-02-0; $ClCH_2CH_2CH_2Cl$, 142-28-9; Cy_2PLi, 19966-81-5; NaP(H)Ph, 51918-31-1; $PhPH_2$, 638-21-1; $CH_2{=}CHCH_2NH_2$, 107-11-9; $CH_2{=}CHSi(OEt)_3$, 78-08-0; $PhP(CH{=}CH_2)_2$, 26681-88-9; o-$NH_2C_6H_4SH$, 137-07-5; $NCCH_2CH_2PH_2$, 6783-71-7; $CH_2{=}CHPPh_2$, 2155-96-6; $CH_2{=}CHCH_2N(CH_3)_2$, 2155-94-4; $CH_2{=}CHCH_2OPh$, 1746-13-0; $PhLiPCH_2CH_2CH_2NH_2$, 71766-70-6; $BrCH_2CH_2CH_2Br$, 109-64-8; trimethylene sulfide, 287-27-4; $PhHPCH_2CH_2CH_2SLi$, 71734-69-5; $PhPLi_2$, 13595-56-7; RhCl(etp-CN), 71733-88-5; $CoCl_2$(etp-CN), 71733-89-6; [PtCl(PPN)]AsF_6, 71733-91-0; RhCl(PPN), 71733-92-1.

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Phosphorus-31 NMR Study of Rhodium Poly(phosphine) Nitrosyl Complexes. An Attempt To Prepare the Elusive Example of a Planar $\{MNO\}^{10}$ Complex Containing a Bent Nitrosyl Ligand

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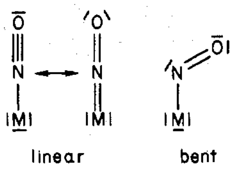
Displacement of triphenylphosphine from $Rh(PPh_3)_3NO$ by chelating bis(phosphine), tris(phosphine), and tetrakis(phosphine) ligands produces a series of new complexes of formulation $RhL_n(PPh_3)_{3-n}NO$, where L_n corresponds to a poly(phosphine) ligand containing n phosphine groups. On the basis of phosphorus-31 NMR spectroscopy, all of these complexes have a pseudotetrahedral inner coordination sphere around rhodium. They appear to have nearly linear Rh–N–O linkages. The potentially tridentate ligand $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2NMe_2$ displaces only two triphenylphosphine ligands from $Rh(PPh_3)_3NO$, as the $-NMe_2$ group remains nonbonded in solution. At −40 °C the potentially tetradentate ligand $P(CH_2CH_2PPh_2)_3$ functions as a tridentate in which one of the terminal $-PPh_2$ groups is nonbonded. However, at higher temperatures, all three terminal diphenylphosphino groups undergo exchange. A line-shape analysis of the ^{31}P NMR spectra gives $\Delta G^{\ddagger} = 8.6$ kcal/mol and $\Delta S^{\ddagger} = -17.2$ eu which indicates that the exchange occurs via an associative mechanism and suggests the transient formation of the "supersaturated" 20-electron, five-coordinate complex $Rh(PP_3)NO$. Complexes of the type $Rh(R_2P(CH_2)_nPRR')(PPh_3)NO$ are chiral at the rhodium atom. Use of a diphosphine ligand containing a chiral substituent on one phosphorus atom (i.e., (2-(diphenylphosphino)ethyl)neomenthylphenylphosphine) shows that the phosphorus resonance is affected more by the chiral carbon substituent than by the chiral nature of the rhodium atom. Trends among the phosphorus–rhodium and phosphorus–phosphorus coupling constants are discussed in relation to the oxidation state of rhodium and the number and size of any chelate rings in the $RhL_n(PPh_3)_{3-n}NO$ complexes.

Introduction

Judging by the number of articles and reviews[1] that have appeared in recent years concerning the coordination chemistry of nitric oxide, it is one of the most vigorous research areas. Catalytic reduction of nitrogen oxides (NO, NO_2, etc.) by homogeneous systems[1d] appears to be promising. The potential role of the nitrosyl moiety (NO) as an electron sink comparable to the $\pi \rightleftarrows \sigma$ interconversion of allyl ligands has also been recognized as being pertinent to various catalytic cycles.[2] Moreover, theoretical questions about the structure, bonding, and reactivity of the metal–nitrosyl linkage continue to create controversy.

The bonding of NO to a metal complex spans a range of M–N–O angles from 120 to 180°.



Interconversion between these extreme geometries is believed to be necessary for activation of the nitrosyl group in the catalytic reduction by CO,[3] but unequivocal evidence for conversion of linear into bent NO is known for only two reactions,[4] both of which involve coordination of an additional

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(1) (a) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974); (b) R. Hoffmann, M. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, **13**, 2666 (1974); (c) K. G. Caulton, *Coord. Chem. Rev.*, **14**, 317 (1975); (d) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975); (e) F. Bottomley, *Coord. Chem. Rev.*, **26**, 7 (1978).

(2) (a) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Am. Chem. Soc.*, **91**, 5659 (1969); (b) M. C. Rakowski, F. J. Hirsekorn, L. S. Stahl, and E. L. Muetterties, *Inorg. Chem.*, **15**, 2379 (1976).

(3) D. E. Hendrickson, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **16**, 970 (1977).

(4) (a) J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, **14**, 624 (1975); (b) J. H. Enemark, R. D. Feltham, B. T. Huie, P. L. Johnson, and K. B. Swedo, *J. Am. Chem. Soc.*, **99**, 3285 (1977).

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ligand. Infrared data have been interpreted to support an equilibrium between a bent and a linear Co–NO bond in $CoCl_2(NO)(PMePh_2)_2$,[5] but alternate interpretations[6] have been proposed.

The class of metal nitrosyl complexes designated[7] as $\{MNO\}^{10}$ can adopt either of two geometries of roughly equivalent energy: pseudotetrahedral with a linear nitrosyl or square-planar containing a bent nitrosyl.[1a,8] Of the structurally characterized members of this class, all but three have strictly linear M–N–O angles. The exceptions, $Ni(NO)(NCS)(PPh_3)_2$,[9] $Ni(NO)(N_3)(PPh_3)_2$,[10] and $Rh(NO)(PPh_3)_3$,[11] have M–N–O angles of 161.5 (5)°, 153 (1)°, and 157 (2)°, respectively, and cannot be considered to be "strongly" bent. A $\{MNO\}^{10}$ complex containing a strongly bent nitrosyl was sought to demonstrate the amphoteric nature of the NO ligand. Recently, an equilibrium between square-planar and tetrahedral geometries was postulated for $[Ni(PPh_3)_3(NO)][PF_6]$ on the basis of a low-temperature ^{31}P NMR study.[12] Our goal was to use poly(phosphine) ligands which are known to form dissociatively stable complexes with rhodium and to fit around square-planar geometries[13] to induce the formally $\{MNO\}^{10}$ complex Rh(NO)(triphosphine) to change from a tetrahedral to a square-planar structure, thereby resulting in a bent nitrosyl.

Phosphorus-31 NMR chemical shifts and coupling constants of the new rhodium–nitrosyl complexes are presented and interpreted. Correlations between the oxidation state of the metal, ^{31}P chemical shift, and phosphorus–phosphorus and phosphorus–rhodium coupling constants are discussed. The fluxional behavior of one of these compounds has been studied by ^{31}P NMR, and a mechanism is proposed for exchange of the phosphine ligands.

Experimental Section

Reagents and Chemicals. The ligands bis(3-(dicyclohexylphosphino)propyl)phenylphosphine (Cyttp), bis(3-(diphenylphosphino)propyl)phenylphosphine (ttp), (3-(diphenylphosphino)propyl)(2-(diphenylphosphino)ethyl)phenylphosphine (eptp), (3-(dimethylamino)propyl)(3-(diphenylphosphino)propyl)phenylphosphine (ppn), bis(2-(dimethylphosphino)ethyl)phenylphosphine (dmetp), and (3-(diphenylphosphino)propyl)phenylphosphine (ppH) were synthesized by literature methods.[14] Samples of 1-(diphenylphosphino)-2-(dimethylphosphino)ethane (dmdpe) and (2-(diphenylphosphino)ethyl)neomenthylphenylphosphine (P-P*) were kindly supplied by Professor R. B. King of the University of Georgia. 1,2-Bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), tris(2-(diphenylphosphino)ethyl)phosphine (PP_3), 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (P_2P_2), and bis(2-(diphenylphosphino)ethyl)phenylphosphine (etp) were obtained from either Strem Chemical Co., Danvers, Mass., or Pressure Chemical Co., Pittsburgh, Pa., and were used as obtained. The compound $Rh(PPh_3)_3(NO)$ was prepared by the published procedure.[15] All reagent-grade solvents were dried thoroughly by distillation from appropriate drying agents and degassed by flushing with N_2 for 30 min prior to use.

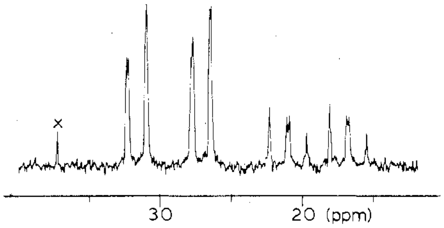

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of Rh(ttp)NO in toluene at 23 °C: x = an impurity; ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$.

Preparation of the Rhodium Nitrosyl Complexes. 1. Rh(ttp)NO. A solution of 825 mg of $Rh(PPh_3)_3NO$ (0.89 mmol) and 3.5 mL of stock ttp solution (1.10 mmol) in 50 mL of benzene was heated under reflux for 15 min. The volume was reduced to 5 mL in vacuo and 50 mL of ethanol was added slowly. After 12 h, red-brown crystals formed on the walls of the flask; the crystals were collected on a filter, washed with 10 mL of ethanol, and dried in vacuo; yield 512 mg (83%). Anal. Calcd for $C_{36}H_{37}NOP_3Rh$: C, 62.16; H, 5.37; N, 2.01; O, 2.30. Found: C, 61.49; H, 5.53; N, 1.91; O, 3.06.

2. Rh(dppp)PPh$_3$(NO). A solution of 871 mg of $Rh(PPh_3)_3NO$ (0.95 mmol) and 420 mg of $Ph_2PCH_2CH_2CH_2PPh_2$ (1.02 mmol) in 50 mL of benzene was heated under reflux for 30 min. The solution was cooled, and 75 mL of ethanol was added to precipitate the brown microcrystalline product, yield 611 mg (76%).

Anal. Calcd for $C_{45}H_{41}NOP_3Rh$: C, 66.91; H, 5.13; N, 1.74. Found: C, 66.79; H, 4.96; N, 1.53.

3. Rh(L$_n$)(PPh$_3$)$_{3-n}$NO Complexes in Situ. Equimolar quantities of $Rh(PPh_3)_3NO$ and the desired polydentate phosphine ligand were dissolved in benzene (or toluene) and heated under reflux for 15 min. The resulting red-brown solution was transferred via a syringe into a 10-mm NMR tube for ^{31}P NMR spectroscopy. The following ligands were employed in this manner: L_2: $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2CH_2CH_2PPh_2$, $Ph_2PCH_2CH_2PMe_2$, $Ph_2PCH_2CH_2CH_2P(Ph)H$, $Ph_2PCH_2CH_2P(Ph)$-*neo*-$C_{10}H_{19}$, $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2NMe_2$; L_3: $PhP(CH_2CH_2PPh_2)_2$, $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$, $PhP(CH_2CH_2PMe_2)_2$, $PhP(CH_2CH_2CH_2PCy_2)_2$; L_4: $P(CH_2CH_2PPh_2)_3$, $(Ph_2PCH_2CH_2P(Ph)CH_2)_2$.

Characterization. Solid-state infrared spectra were measured on a Perkin-Elmer 337 or 457 grating spectrophotometer from 400 to 4000 cm^{-1} and 250 to 4000 cm^{-1}, respectively, as Nujol mulls, pressed potassium bromide pellets, or solutions as indicated. Sharp polystyrene absorptions at 1601 and 906.7 cm^{-1} were used for calibration. Fourier-mode, proton-noise-decoupled, phosphorus-31 nuclear magnetic resonance spectra were collected on a Bruker HX90 spectrometer operating at 36.43 MHz with a Bruker B-NC 12 data system. Ten-millimeter tubes with concentric 5-mm inserts (containing the deuterium lock and trimethyl phosphate as a secondary standard) were used for the ^{31}P spectra; the chemical shifts and coupling constants are reproducible to ±0.05 ppm and ±1.0 Hz, respectively. Phosphorus-31 chemical shifts are reported in ppm from 85% H_3PO_4; positive chemical shifts are downfield from the phosphorus standard.

Results and Discussion

Substitution of poly(phosphine) ligands for triphenylphosphine in the complex $Rh(PPh_3)_3NO$ proceeds smoothly in refluxing benzene or toluene and the substituted complexes, $RhL_n(PPh_3)_{3-n}(NO)$, can be precipitated as red-brown solids in most cases by addition of ethanol. However, for several compounds, where L_n = a bidentate phosphine, the original compound $Rh(PPh_3)_3NO$, crystallizes upon addition of alcohol, suggesting that an equilibrium exists in solution between the substituted complex and $Rh(PPh_3)_3NO$ as shown in eq 1. The

$$Rh(PPh_3)_3NO + PP \rightleftarrows Rh(PP)(PPh_3)NO + 2PPh_3 \qquad (1)$$

^{31}P NMR spectra show that in benzene this equilibrium lies far to the right (vide infra); however, upon addition of alcohol,

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(5) (a) C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, **12**, 1304 (1973); (b) J. P. Collman, P. H. Farnham, and G. Dolcetti, *J. Am. Chem. Soc.*, **93**, 1788 (1971).

(6) Reference 1a, p 396.

(7) The classification $\{MNO\}^x$ was introduced by Enemark and Feltham[1a] to represent a metal–nitrosyl compound in which the nitrosyl is formally considered to be NO^+ and the metal to have *x* d electrons. This convention avoids the problem of assigning to the metal oxidation states that are often misleading.

(8) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1209 (1973).

(9) K. J. Haller and J. H. Enemark, *Inorg. Chem.*, **17**, 3552 (1978).

(10) J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971).

(11) J. A. Kaduk and J. A. Ibers, *Isr. J. Chem.*, **15**, 143 (1977).

(12) S. Bhaduri, B. F. G. Johnson, and T. W. Matheson, *J. Chem. Soc., Dalton Trans.*, 561 (1977).

(13) T. E. Nappier, Jr., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 4194 (1973).

(14) K. D. Tau, R. J. Uriarte, T. J. Mazanec, and D. W. Meek, *Inorg. Chem.*, companion paper in this issue.

(15) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 2947 (1970).

Table I. Phosphorus-31 NMR Data for $RhL_n(PPh_3)_{3-n}(NO)$ Complexes

	chemical shifts, ppm			coordination chemical shifts, ppm			coupling constants, Hz					
L_n	$\delta(P_1)$	$\delta(P_2)$	$\delta(P_3)$	$\Delta(P_1)$	$\Delta(P_2)$	$\Delta(P_3)$	Rh–P_1	Rh–P_2	Rh–P_3	P_1–P_2	P_1–P_3	P_2–P_3
PPh_3[a,b]	48.8			54.6			175					
ttp[c]	18.8		29.2	47.6		46.2	154		164		48	
etp[d]	89.3	69.7		105.9	82.5		154	167		18		
eptp[c,d]	56.0	68.9	30.2	78.4	82.1	48.3	156	166	169	12	45	0
dppp[b,c]	52.2		27.9	58.0		45.2	178		162		12	
ppH[b,e]	53.3	2.3	30.2	59.1	56.8	48.2	171	160	167	26	10	49
ppn[b,e]	52.4	18.6	30.7	58.2	45.8	48.9	175	160	161	19	12	52
dmetp[d]	94.3	34.3		112.5	83.2		151	166		12		
Cyttp[c]	27.6		37.2	55.7		45.0	153	163			49	
dmdpe[b,e]	51.2	65.6	31.0	57.0	82.2	82.1	171	163	170	7	17	14
dppb[b,f]	50.7	39.2		56.6	57.2		176	169		9		
PP_3[d,g]	93.4	71.5	−16.3	110.9	84.6		148	164		22	34	0
P-P*[b,e,h]	48.6	[i]	65.8	54.4	[j]	81.5	175	164	155			

[a] Data from ref 18. [b] P_1 represents the PPh_3 group(s). [c] P_3 represents the phosphorus atom(s) at the end of the trimethylene chain. [d] P_2 represents the phosphorus atom(s) at the end of the ethylene chain. [e] P_3 is the PPh_2 group. [f] P_2 are the two phosphorus atoms of dppb. [g] P_3 is the dangling PPh_2 group. [h] P_2 is the chiral phosphorus group. [i] The enantiomers produce two different sets of resonances for $\delta(P_2)$. [j] Due to the two sets of peaks for P_2, $\Delta(P_2)$ values are not reported for the chiral phosphorus group.

the less soluble compound $Rh(PPh_3)_3NO$ precipitates. Owing to the difficulty of isolating the Rh–NO complexes of the polyphosphines, several of these reactions were studied in situ.

The red-brown solid that was isolated by treating $Rh(PPh_3)_3NO$ with the tridentate phosphine $PhP(CH_2CH_2CH_2PPh_2)_2$ (ttp) gave the ^{31}P NMR spectrum shown in Figure 1. The spectrum can be interpreted as the A_2B portion of an A_2BX spectrum (X = ^{103}Rh, 100% abundant, $I = ^1/_2$. The NMR parameters of this complex and the others are listed in Table I. Metal–phosphorus coupling constants are known to *decrease* with *increasing* oxidation state and increasing coordination number of the metal,[16] so a significant decrease from the only reported value of a one-bond coupling constant for phosphorus to Rh(–I)[17] [175 Hz in $Rh(PPh_3)_3NO$][18] was expected to indicate planar Rh(I). However, the observed $^1J_{Rh-P}$ values of 154 and 164 Hz in Rh(ttp)NO are in the range for either Rh(I) or Rh(–I). Further, the equivalence of the two terminal phosphorus atoms does not differentiate between planar or pseudotetrahedral structures.

The nitrosyl stretching frequency has been suggested as a diagnostic tool for discriminating between linear and bent NO ligands,[19] although overlap occurs in the region 1600–1720 cm^{-1}. The infrared spectrum of Rh(ttp)NO in the NO stretching region is similar to that of $Rh(PPh_3)_3NO$; there is a strong band at 1610 cm^{-1} with a medium shoulder at 1595 cm^{-1}. This absorption band is in the uncertain region, even if one applies various "correction factors".[20] On this basis it is impossible to predict accurately the RhNO angle in Rh(ttp)NO, particularly in view of the unusual RhNO angle of 157° found for $Rh(PPh_3)_3NO$.[11]

In an attempt to clarify the uncertainty of the RhNO angle in Rh(ttp)NO, the symmetrical bidentate ligand dppp (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) was used. In this case we expected the resulting ^{31}P NMR spectrum of $Rh(dppp)(PPh_3)NO$ to differentiate between pseudotetrahedral (an A_2MX ^{31}P pattern) and square-planar (an ABMX ^{31}P pattern) geometries.

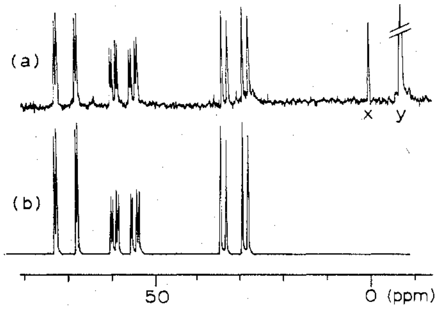
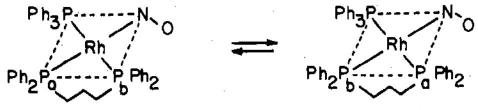


Figure 2. (a) Experimental $^{31}P\{^1H\}$ NMR spectrum of Rh(eptp)NO in toluene at 23 °C: eptp = $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2$; x = the $(MeO)_3PO$ secondary standard and y = PPh_3. (b) Computer-simulated spectrum of Rh(eptp)NO, with the parameters listed in Table I.

The A_2MX pattern that results in the experimental ^{31}P NMR spectrum remains invariant down to −50 °C; thus, we are faced with two possibilities: (1) the complex is pseudotetrahedral or (2) a rapid equilibrium exists between the two equivalent planar structures even at low temperature as shown in eq 2.



(2)

Although such an equilibration of the two planar isomers is possible, it is highly unlikely since the $^2J_{P_1-P_3}$ value is only ±12 Hz. If the equilibrium were rapid, $^2J_{P_1-P_3}$ should be an average of $^2J_{P-P}$(trans) and $^2J_{P-P}$(cis), which are typically in the range 250–400 Hz and −10 to −50 Hz, respectively, for analogous planar Rh(I) complexes.[16b]

To lower the symmetry that is imposed by the two symmetric ligands discussed above, we used the unsymmetrical tris(tertiary phosphine) eptp (eptp = $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2$) in the displacement reaction. Also, for direct comparison purposes, the symmetrical triphosphine ligand $PhP(CH_2CH_2PPh_2)_2$, etp, which contains ethylene chains, was used to prepare Rh(etp)NO. The ^{31}P NMR spectrum of Rh(eptp)NO in situ is presented in Figure 2 along with a computer simulation of the spectrum. The parameters for the Rh(eptp)NO and Rh(etp)NO complexes are listed in Table I. By comparison with the spectra of Rh(ttp)NO and Rh(etp)NO, the three phosphorus resonances in Rh(eptp)NO can be assigned unequivocally to the fragments $Ph_2PCH_2CH_2$– ($\delta(P_2)$ = 68.9), $Ph_2PCH_2CH_2CH_2$– ($\delta(P_3)$ = 30.2), and –P(Ph) ($\delta(P_1)$ = 56.0). The spectrum is very nearly first order

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(16) (a) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969); (b) P. R. Blum, Ph.D. Dissertation, The Ohio State University, Dec 1977.

(17) The nitrosyl group, which is nearly linear, is formally considered to be NO^+, making the formal oxidation state of rhodium –I in $Rh(PPh_3)_3NO$. We recognize that this is somewhat artificial in view of the covalent nature of M–NO bonds.

(18) K. G. Caulton, *Inorg. Chem.*, **13**, 1774 (1974).

(19) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1479 (1971).

(20) (a) A. P. Gaughan, Jr., B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, Jr., and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 6859 (1973); (b) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975).

with ${}^1J_{Rh-P}$ values comparable to those of Rh(ttp)NO and Rh(dppp)NO and ${}^2J_{P-P}$ values of 12.5 ($J_{P_1-P_2}$), 45.3 ($J_{P_1-P_3}$), and 0.0 ($J_{P_2-P_3}$) Hz. The coupling constants between phosphorus atoms in the same five- and six-member chelate rings closely match those in the symmetrical ligands. The unexpected value of ~0.0 Hz for coupling between the terminal phosphorus atoms is not compatible with a trans arrangement, in which ${}^2J_{P-P}$ is usually in the range 250–400 Hz.[16b] Computer simulation employing values as high as 500 Hz for ${}^2J_{PPh_2-PPh_2}$ did not yield an acceptable fit to the data. Although the phosphorus–phosphorus coupling constants apparently establish the structure as pseudotetrahedral for Rh(eptp)NO (and by analogy for all of the above complexes), the ${}^2J_{P_2-P_3}$ value of zero is disturbing.

The ~0 Hz coupling between P_2 and P_3 in Rh(eptp)NO might indicate that the P_2–M–P_3 angle is the critical angle at which the sign of ${}^2J_{P-P}$ changes from the small, negative couplings for cis (90°) geometry (i.e., −52 Hz in RhCl(ttp)) to the large, positive coupling constants for mutually trans phosphines (i.e., ${}^2J_{P_2-P_3}$ = 362 Hz in RhCl(eptp) (vide infra) where the angle P_2–M–P_3 is expected to be close to 180°).[16b] Without detailed knowledge of the absolute signs of the phosphorus–phosphorus coupling constants and the P–M–P angles, a definitive conclusion cannot be made at this time.

Owing to the anomalously low value of ${}^2J_{PPh_2-PPh_2}$ for Rh(eptp)NO, we investigated another example in which all three phosphorus atoms are different. Thus, the unsymmetrical bidentate ligand $Ph_2PCH_2CH_2CH_2P(H)Ph$, ppH, was used and the ${}^{31}P$ NMR spectrum of its in situ product is presented in Figure 3, along with its computer simulation. The parameters, listed in Table I, are comparable to the other complexes. Again, it is especially significant that all three ${}^2J_{P-P}$ values are small (i.e., ${}^2J_{P_1-P_2}$ = 26.0, ${}^2J_{P_1-P_3}$ = 9.6, and ${}^2J_{P_2-P_3}$ = 49.0 Hz). The infrared spectrum in benzene shows ν(NO) at 1605 cm^{-1}, again accompanied by a broad shoulder at slightly lower energy. Both the NMR and infrared data are consistent with a pseudotetrahedral complex.

Variation of the substituents on phosphorus can drastically alter the σ-donating ability and the steric properties of a ligand. By changing the substituents from phenyl to alkyl groups, we tried to increase the electron density on rhodium to such an extent that the metal might possibly change from a σ acceptor to a σ donor with respect to the nitrosyl moiety. Changing the donor–acceptor role of rhodium would correspond to formal oxidation of Rh(−I) to Rh(+I) and formal reduction of NO$^+$ to NO$^-$, which would require the MNO linkage to bend strongly and demonstrate its amphoteric nature. Three ligands were employed for this purpose: Cyttp, dmetp, dmdpe. The ${}^{31}P$ NMR data are collected in Table I; clearly, the rhodium–phosphorus and phosphorus–phosphorus coupling constants indicate that these complexes are pseudotetrahedral (vide supra). Interestingly, ${}^2J_{P_1-P_2}$ in Rh(dmdpe)(PPh$_3$)NO (coupling between PPh$_3$ and Ph$_2$P–) is only 7.0 Hz, perhaps indicating that the anomalous value of 0.0 Hz in Rh(eptp)NO is "real", although still not rationalized definitively. The infrared absorptions assigned to the NO group in the spectra of these complexes in benzene are similar to that of Rh(PPh$_3$)$_3$NO.

Another possibility to induce bending of the RhNO linkage is to use a tetradentate P_4 ligand. If all four of the phosphine groups are attached to the metal, the Rh–NO linkage would necessarily bend to avoid forming a "supersaturated" 20-electron species. Two commercially available branched and open-chain ligands PP$_3$ and P$_2$P$_2$ (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$; P$_2$P$_2$ = [Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$]$_2$) were used. Since the PP$_3$ ligand was studied in more detail, those results will be discussed here. The in situ reaction mixture formed from Rh(PPh$_3$)$_3$NO and PP$_3$ in toluene gave the ${}^{31}P$ NMR spectra shown in Figure 4 over the temperature range −40 to +30 °C. At −40 °C the spectrum indicates a "frozen" structure in which the PP$_3$ ligand is functioning as a tridentate ligand with one of the terminal Ph$_2$P– groups unbonded as illustrated in **1**. The ${}^{31}P$ NMR assignments are as follows: $\delta(P_a)$ = 93.4 (d of d of t), $\delta(P_b)$ = 71.5 (d of d), $\delta(P_c)$ = −16.3 (d), J_{ab} = 21.9 Hz, J_{ac} = 33.6 Hz, J_{P_a-Rh} = 148.4 Hz, and J_{P_b-Rh} = 163.6 Hz. As the temperature is raised, the bonded and free Ph$_2$P– groups (b–c) begin to exchange positions as evidenced by the simultaneous broadening of these resonances. They eventually give rise to a weak, broad absorption at ca. 40 ppm at 50 °C, the highest temperature studied (not shown). The resonance due to the central phosphorus atom, P_a, broadens but never loses its

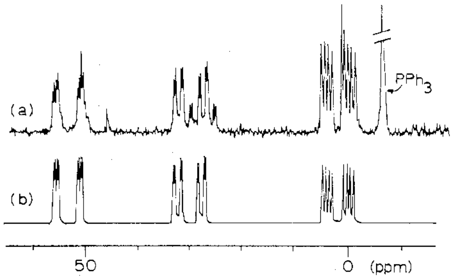


Figure 3. (a) Experimental ${}^{31}P\{{}^1H\}$ NMR spectrum of Rh(ppH)(PPh$_3$)NO in toluene at 23 °C: ppH = Ph$_2$PCH$_2$CH$_2$CH$_2$P(H)Ph. (b) Computer-simulated spectrum of Rh(ppH)(PPh$_3$)NO with the parameters listed in Table I.

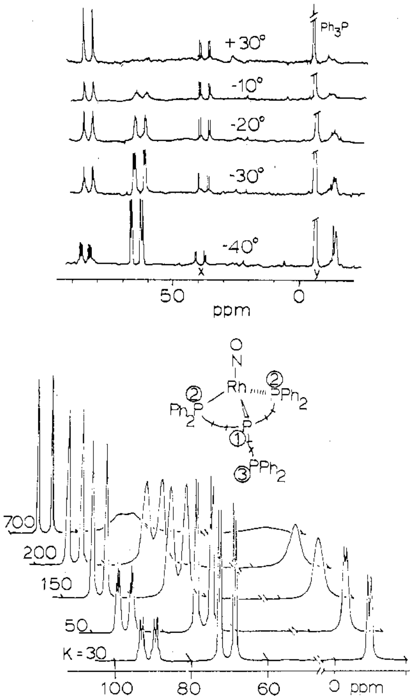
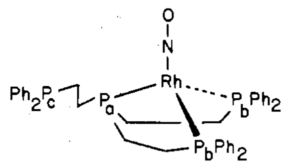


Figure 4. Top: Variable temperature ${}^{31}P\{{}^1H\}$ NMR spectra of Rh(PP$_3$)NO in toluene; x = an impurity; the strong signal of y results from the displaced Ph$_3$P ligands. Bottom: Line-shape analysis of ${}^{31}P\{{}^1H\}$ spectra of Rh(PP$_3$)NO: PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$; the "best fit" coupling constants used for the computer simulation are ${}^1J_{P_2-Rh}$ = 163, ${}^1J_{P_1-Rh}$ = 148, ${}^3J_{P_1-P_3}$ = 34, and ${}^2J_{P_1-P_2}$ = −23 Hz.



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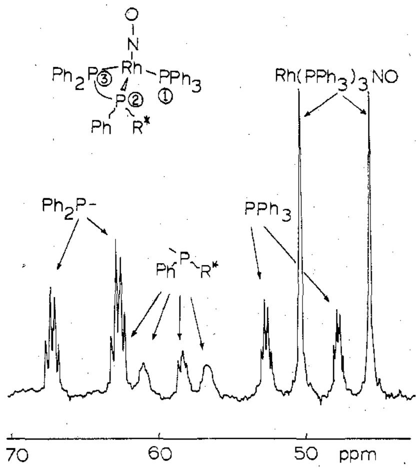


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $Rh(P\text{-}P^*)(PPh_3)NO$ in toluene at 23 °C: P-P* = the chiral ligand $Ph_2PCH_2CH_2CH_2P(Ph)$-*neo*-$C_{10}H_{19}$.

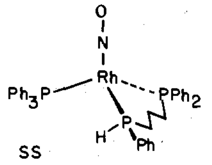
coupling to the ^{103}Rh nucleus, indicating that it does not become detached from the rhodium.[21]

Caulton[18] employed ^{31}P NMR spectroscopy to determine that free PPh_3 exchanged with $Rh(PPh_3)_3NO$ via a dissociative mechanism. Owing to the strong chelating tendency of poly(phosphine) ligands and the associative mechanism proposed for $Pt(CH_3)_2$(poly(phosphine)) complexes,[22] it seemed likely that the exchange of the $-PPh_2$ groups in $Rh(PP_3)NO$ proceeded via an associative mechanism rather than the dissociative mechanism proposed for $Rh(PPh_3)_3NO$.

A line-shape analysis of the ^{31}P NMR spectra with the DNMR program[23] was undertaken to provide detailed information about the exchange mechanism. Some of the representative computed spectra are presented in Figure 4 along with the experimental spectra. A linear Arrhenius plot of the data yields $\Delta G^{\ddagger} = 8.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17.2$ eu. The large negative value of the activation entropy suggests an associative mechanism, indicating that all four phosphorus atoms are bonded to the rhodium in the intermediate. Such a complex is the 20-electron species that was sought. The infrared spectrum of $Rh(PP_3)NO$ in solution shows ν(NO) at 1615 cm^{-1}, accompanied by the usual shoulder at 1595 cm^{-1}. The infrared spectrum contains no evidence for the bent form of the nitrosyl; perhaps it is present only in small concentration or it is obscured by overlap with ligand absorptions. If the nitrosyl group really is bent in the intermediate, $Rh(PP_3)NO$ may be a candidate as a catalyst for the reduction of NO.

One could raise the question whether a chelating amine would displace PPh_3 from $Rh(PPh_3)_3NO$. Thus, the open-chain tridentate, $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2N(CH_3)_2$, ppn, was employed in the displacement reaction. The ^{31}P NMR parameters listed in Table I indicate that PPh_3 was not displaced by the chelating amine group, at least in the presence of excess PPh_3; ppn functions as a bidentate ligand with a dangling amino group. The preference of rhodium for phosphorus vs. nitrogen donors suggests that there may be a significant bonding contribution from dπ (Rh→P) overlap which is not available for nitrogen donors. Similar results have been found for other Rh(I), Pd(II), and Pt(II) compounds.[24]

In the complex $Rh(ppH)(PPh_3)NO$ one phosphorus atom and the rhodium atom are bonded to four different groups; hence both phosphorus and rhodium are chiral centers. The two chiral centers should give rise to two diastereomerically related pairs of enantiomers as in **2**–**5**. The two enantiomeric pairs should possess different chemical and physical properties, but this is not observed in the ^{31}P NMR spectrum (Figure 3). One rationalization of the spectrum is that the *RR/SS* pair, **2** and **3**, is formed preferentially instead of the *RS/SR* pair, **4** and **5**, in order for the sterically large phenyl group to avoid the proximity of the bulky PPh_3 ligand. Of course, it is also possible for the diastereomers to have accidentally equivalent ^{31}P NMR parameters.



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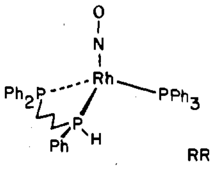

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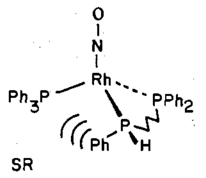

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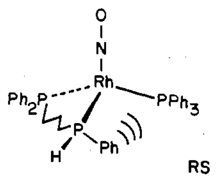

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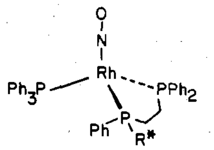
A ligand containing a chiral substituent on phosphorus is required to solve this problem. A small sample of such a ligand, (2-(diphenylphosphino)ethyl)neomenthylphenylphosphine (P-P*), was obtained from Professor R. B. King, and the reaction of this ligand with $Rh(PPh_3)_3NO$ in toluene was studied by ^{31}P NMR spectroscopy. The resulting complex, $Rh(P\text{-}P^*)(PPh_3)NO$, has three chiral centers: rhodium, phosphorus, carbon. The chirality at the carbon atom is fixed; hence, the resulting complex can exist in four diastereomeric forms, **6**–**9**, none of which are mirror images. Thus, in theory, the resulting ^{31}P NMR spectrum could show a mixture of four compounds.



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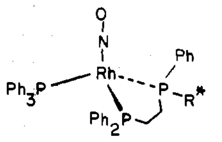

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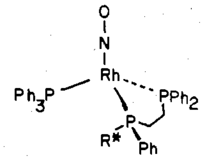

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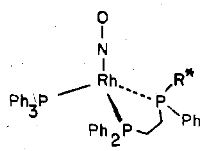

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[21] The doublet of doublets centered at 42.2 ppm in the ^{31}P NMR spectrum of $Rh(PP_3)NO$ is the M_3 portion of an AM_3X pattern ($\delta(P_A) = 134.5$, $\delta(P_M) = 42.2$, $J_{P_A-P_M} = 19$ Hz, $J_{P_A-Rh} = 107$ Hz, $J_{P_M-Rh} = 155$ Hz, X = ^{103}Rh). Although this impurity has not been positively identified, on the basis of the ^{31}P NMR spectrum, the PP_3 ligand exhibits a C_{3v} structure. Perhaps the NO ligand has been converted to NO_2. The compound $RhCl(PP_3)$ exhibits a very similar ^{31}P NMR spectrum ($\delta(P_A) = 146.5$, $\delta(P_M) = 40.0$, $J_{P_A-P_M} = 18$ Hz, $J_{P_A-Rh} = 126$ Hz, $J_{P_M-Rh} = 149$ Hz, X = ^{103}Rh), but the ^{31}P NMR spectrum of $Rh(NO_3)(PP_3)$ appears as an ADM_2X pattern ($\delta(P_A) = 149.6$, $\delta(P_D) = 51.9$, $\delta(P_M) = 35.3$, $J_{P_A-P_D} \simeq J_{P_A-P_M} \simeq 0$ Hz, $J_{P_D-P_M} = 20$ Hz, $J_{P_A-Rh} = 98$ Hz, $J_{P_D-Rh} = 120$ Hz, $J_{P_M-Rh} = 89$ Hz, X = ^{103}Rh) indicating only C_s symmetry and precluding that this might be the impurity in $Rh(PP_3)NO$: T. J. Mazanec and D. W. Meek, unpublished results.

[22] (a) K. D. Tau, R. Uriarte, T. J. Mazanec, and D. W. Meek, *J. Am. Chem. Soc.*, **101**, 6614 (1979); (b) K. D. Tau and D. W. Meek, *J. Organomet. Chem.*, **139**, C83 (1977).

[23] D. A. Klein and G. Binsch, "DNMR3: A Computer Program for the Calculation of Complex Exchange-Broadened NMR Spectra. Modified Version for Spin Systems Exhibiting Magnetic Equivalence or Symmetry", Program 165, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. 1970.

[24] (a) T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, **96**, 3098 (1974); (b) C. A. McAuliffe, "Transition Metal Complexes of P, As, and Sb Ligands", Wiley-Interscience, New York, 1973, p 27.

Table II. Phosphorus-31 NMR Coordination Chemical Shifts in $RhL_n(PPh_3)_{3-n}(NO)$ Complexes

	Δ^a	$\Delta_R{}^b$	no. of obsvn
PPh_3	57.4 ± 1.7	0	5
5-member ring	82.2 ± 1.0	+24.8	8
6-member ring	46.7 ± 1.6	−10.7	7
7-member ring	57.2	~0	1
two 5-member rings	109.8 ± 3.4	+52.4	3
two 6-member rings	51.6	−5.8	2

^{a} $\Delta = \delta(\mathrm{P_{coordinated}} - \delta(\mathrm{P_{free\ ligand}})$. ^{b} $\Delta_R = \Delta - \Delta(PPh_3)$.

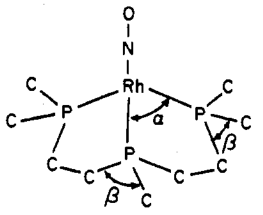
Table III. Correlation between Chelation and Rhodium–Phosphorus Coupling Constants for $RhL_n(PPh_3)_{3-n}(NO)$ Complexes

P environmt	$^1J_{Rh-P}$, Hz range	$^1J_{Rh-P}$, Hz mean	no. of obsvn
no chelate rings	170–178	174.1 ± 3.2	6
one chelate ring	160–171	164.4 ± 3.6	14
two chelate rings	148–156	152.6 ± 2.7	6

The experimental $^{31}P\{^1H\}$ NMR spectrum is presented in Figure 5. The two sharp single peaks centered at 48.8 ppm are due to excess $Rh(PPh_3)_3NO$ and can be neglected. The remainder of the spectrum shows four doublets of multiplets in the ratio 2:1:1:2 centered at 65.7, 61.2, 59.7, and 50.8 ppm (part of the multiplet at 61.2 ppm is obscured by the right half of the 65.7 ppm multiplet). The multiplets farthest downfield and upfield can be assigned to the Ph_2P- and PPh_3 groups, respectively, by comparison of the chemical shifts with other similar complexes in Table I. Thus, the phosphorus atom containing the chiral neomenthyl group directly bonded to it is the only one for which more than one diastereomer can be differentiated on the basis of the ^{31}P NMR spectrum. Observation of two diastereomers can be due to the effect of the chirality at either rhodium or phosphorus. If the chiral metal causes the inequivalence of the ^{31}P chemical shifts, why are the other phosphorus atoms not affected similarly? Since they are not affected, we have concluded that the chirality *at phosphorus* must cause the two widely separated multiplet patterns. Close examination of the individual multiplets reveals that they are not so well resolved as the multiplets due to the $-PPh_2$ or PPh_3 ligands. Perhaps this broadening results from a very small difference in the chemical shift at the chiral phosphorus due to the influence of the chiral rhodium atom. In a similar study, we found the difference in chemical shifts for the phosphorus atom directly bonded to the chiral group in the two diastereomers of $PtMe_2(P\text{-}P^*)$ was 4.5 ppm, whereas the phosphorus at the other end of the chain experienced a difference of only 1.0 ppm.[22a]

The ^{31}P resonance of a phosphorus group generally shifts when the group is coordinated to a metal; the coordination chemical shift, Δ, has been defined as $\delta(^{31}P_{coordinated}) - \delta(^{31}P_{free\ ligand})$. The magnitude of Δ varies in a predictable fashion and depends on the number and size of any chelate rings in which the phosphorus atom is located.[25] The so-called "ring contribution" to this shift, Δ_R, depends primarily on ring size within a series of analogous complexes.[26] Values of Δ and Δ_R are summarized in Table II for the $RhL_n(PPh_3)_{3-n}(NO)$ complexes studied here. The contributions of two five-membered rings are additive; the phosphorus in both five-membered rings in Rh(etp)NO has a Δ_R value about twice as large as Δ_R for the phosphorus atoms in only one chelate ring (48.5 ppm vs. 25.1 ppm). The effects do not appear to be additive for six-member rings. The lone example of a phosphorus in a seven-member ring exhibited $\Delta_R \simeq 0$. Although ring strain and the concomitant change in the hybridization around phosphorus have been invoked to account for the shift due to the presence of chelate rings,[25b,27] no satisfactory explanation has been given for the substantially larger deshielding effect observed for phosphorus atoms in a five-member ring as compared to four-, six-, and seven-member ring analogues.

The one-bond rhodium–phosphorus coupling constants, $^1J_{Rh-P}$, are also sensitive to chelation, as shown in Table III. This was not surprising, but the trend of *decreasing* coupling with an *increasing* number of chelate rings was unexpected. This trend is also independent of the size of the chelate ring (for five- and six-member rings) and the nature of substituents on phosphorus. It is tempting to correlate the reduced rhodium–phosphorus coupling on chelation with the strain in the tetrahedral coordination angles around the metal due to the limited "chelate-bite angles". As the P–Rh–P angles (α in **10**) decrease from the ideal tetrahedral angle of 109.5°, the s character of the metal orbitals involved in metal–phosphorus bonding decreases, which is predicted to reduce the metal–phosphorus coupling. Thus, $^1J_{Rh-P}$ should decrease as the "chelate-bite-angle" is reduced by using a shorter chain in the chelating ligand, but very little difference and/or trend is observed between ligands with ethylene (av $^1J_{Rh-P}$ = 165.9 Hz), trimethylene (av $^1J_{Rh-P}$ = 163.3 Hz), and tetramethylene ($^1J_{Rh-P}$ = 169 Hz) connecting chains. Perhaps $^1J_{Rh-P}$ more strongly reflects the strain in the C–P–C angles (β in **10**) which may be distorted to about the same extent in all of these compounds, since even the seven-member ring appears to be insufficient to span the 109° angle required by a pseudotetrahedral geometry.



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Phosphorus–phosphorus coupling constants in the $RhL_n(PPh_3)_{3-n}(NO)$ series show variations with chelate ring size. Those phosphorus atoms contained in the same six-member chelate ring show the largest $^2J_{P-P}$ values (45–52 Hz), while phosphorus atoms involved in five-member rings are coupled less strongly (12–22 Hz), probably due to opposing signs of "through-the-metal" and "through-the-chelate-ring" couplings.[25] Surprisingly, coordinated PPh_3, which is consistently coupled most strongly to the metal, is not strongly coupled to the other phosphorus atoms ($^2J_{P-P}$ range 7–26 Hz). Where coupling is limited to the "through-the-metal" mechanism, it is expected to show a strong dependence on the P–M–P angle, α. Within the six-member rings, the P–M–P angles are probably close to 90°; however, the angles between PPh_3 and phosphorus atoms in the bis(phosphine) are free to expand, perhaps even beyond the 102° P–M–P angle observed for $Rh(PPh_3)_3NO$.[11]

Acknowledgment. We thank Professor R. B. King for a small sample of the chiral ligand $Ph_2PCH_2CH_2P(Ph)$-*neo*-$C_{10}H_{19}$, Dr. J. M. Geckle for useful discussions about the line-shape analysis, and the National Science Foundation for

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

(27) R. B. King and J. C. Cloyd, Jr., *Inorg. Chem.*, **14**, 1550 (1975).

an instrument grant that aided in the purchase of the Bruker HX90 NMR spectrometer.

Registry No. $Rh(PPh_3)_3NO$, 21558-94-1; Rh(ttp)NO, 71411-11-5; Rh(etp)NO, 71411-12-6; Rh(eptp)NO, 71411-13-7; Rh(dppp)$(PPh_3)NO$, 71411-14-8; Rh(ppH)$(PPh_3)NO$, 71411-15-9; Rh(ppn)$(PPh_3)NO$, 71411-16-0; Rh(dmetp)NO, 71411-17-1; Rh(Cyttp)NO, 71411-18-2; Rh(dmdpe)$(PPh_3)NO$, 71434-85-0; Rh(dppb)$(PPh_3)NO$, 71411-19-3; $Rh(PP_3)NO$, 71411-20-6; Rh(P-P*)$(PPh_3)NO$, 71411-21-7; $[Rh(ttp)(NO)_2]BF_4$, 71411-23-9.

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Reaction of Hydrogen Peroxide with Metal Complexes. 4.[1] Kinetic Studies on the Peroxo Complex Formation of (Polyaminopolycarboxylato)dioxovanadate(V)

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The kinetics of the reactions of hydrogen peroxide with dioxovanadate(V) complexes of ethylenediamine-*N,N,N′,N′*-tetraacetate (EDTA), ethylenediamine-*N,N′*-diacetate (EDDA), and *N,N′*-dimethylethylenediamine-*N,N′*-diacetate (DMEDDA) have been studied spectrophotometrically at an ionic strength of 1.0 M ($NaClO_4$) in the pH range 3–6 between 15 and 35 °C. With a large excess of H_2O_2 over vanadium(V) complex concentration, a faster reaction followed by a slower one was observed. The rate laws for the fast reactions are $k_1^{\mathrm{DMEDDA}}(1 + K_{\mathrm{as}}^{\mathrm{DMEDDA}}[H_2O_2])^{-1}[VO_2(\mathrm{dmedda})^-][H_2O_2][H^+]$, with $k_1^{\mathrm{DMEDDA}} = (2.0 \pm 0.5) \times 10^3\ M^{-2}\ s^{-1}$ and $K_{\mathrm{as}}^{\mathrm{DMEDDA}} = 300 \pm 100\ M^{-1}$ at 25 °C, for the V(V)–DMEDDA system, and $(k_0^{\mathrm{EDDA}} + k_1^{\mathrm{EDDA}}[H^+])(1 + K_{\mathrm{as}}^{\mathrm{EDDA}}[H_2O_2])^{-1}[VO_2(\mathrm{edda})^-][H_2O_2]$, with $k_0^{\mathrm{EDDA}} = 0.27 \pm 0.04\ M^{-1}\ s^{-1}$ ($\Delta H^{\ddagger} = 49 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -90 \pm 5$ J mol^{-1} K^{-1}), $k_1^{\mathrm{EDDA}} = (2.8 \pm 0.3) \times 10^4\ M^{-2}\ s^{-1}$, and $K_{\mathrm{as}}^{\mathrm{EDDA}} = 20 \pm 10\ M^{-1}$ at 25 °C, for the V(V)–EDDA system. K_{as} refers to a formation constant of an associated complex between H_2O_2 and VO_2L. With an excess of V(V)–EDTA complex over $[H_2O_2]$, the rate law for the peroxo complex formation is $(k_1^{\mathrm{EDTA}}[VO_2(\mathrm{edta})^{3-}] + k_2^{\mathrm{EDTA}}[VO_2(\mathrm{Hedta})^{2-}])[H_2O_2][H^+]$, where $k_1^{\mathrm{EDTA}} = (1.5 \pm 0.1) \times 10^6\ M^{-2}\ s^{-1}$ ($\Delta H^{\ddagger} = 47 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = 29 \pm 8$ J mol^{-1} K^{-1}) and $k_2^{\mathrm{EDTA}} = (4.6 \pm 0.8) \times 10^4\ M^{-2}\ s^{-1}$ ($\Delta H^{\ddagger} = 36 \pm 8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -17 \pm 10$ J mol^{-1} K^{-1}) at 25 °C. This rate expression corresponds to one for the fast reaction with excess H_2O_2 conditions. An associative mechanism through a seven-coordinate transition state is most probably operative.

Introduction

Recently, it has been shown that vanadium, which is essential to mammalian life, may be present in muscle tissue at concentrations sufficient to inhibit the sodium and potassium stimulated adenosine triphosphate.[2] There is increasing evidence that vanadium has a significant biological role.[3-6] Kinetic studies of the formation of peroxovanadium(V) complexes in aqueous solution are scarce.[7,8] The main obstacle appears to be uncertainty regarding the precise nature of the vanadium(V) species present in solution. Previously we have reported kinetics of reaction of hydrogen peroxide and vanadium(V) complexes with monoaminopolycarboxylic acids,[9] such as PDA,[10] NTA,[10] and MIDA.[11] Our attention has been drawn to the reactions of hydrogen peroxide with the vanadium(V)–EDTA family[9] complexes, of which the conformation has been established. The X-ray data for $Na_3[VO_2(\mathrm{edta})]\cdot 4H_2O$[12] and $NH_4[VO_2(H_2\mathrm{edta})]\cdot 3H_2O$[13] have given evidence that two oxygen atoms of the VO_2 unit are in the cis configuration and a nitrogen atom of the coordinated EDTA is in a position trans to the oxo oxygen atom of VO_2 (α-cis in the terminology suggested by Garnett et al.[14]) and that all corresponding bond parameters in the coordination groups of these species are nearly identical. According to an NMR study in aqueous solution the EDTA and DMEDDA complexes form a single isomer (α-cis), while the EDDA complex forms both α-cis and β-cis isomers.[15]

The purpose of the present work is to examine differences in the reactivities of the vanadium(V)–EDTA family complexes for peroxo complex formation and to provide new information on the reaction mechanism. We have also determined the protonation constants of the vanadium(V)–EDTA and its peroxo complexes which are necessary to analyze kinetic results.

Experimental Section

Reagents. Solutions of sodium perchlorate and sodium hydroxide were prepared as described previously.[10] Perchloric acid of special

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(9) Ligand abbreviations: PDA, 2,6-pyridinedicarboxylic acid (H_2pda); NTA, nitrilotriacetic acid (H_3nta); MIDA, *N*-methyliminoacetic acid (H_2mida); EDTA, ethylenediamine-*N,N,N′,N′*-tetraacetic acid (H_4edta); EDDA, ethylenediamine-*N,N′*-diacetic acid (H_2edda); DMEDDA, *N,N′*-dimethylethylenediamine-*N,N′*-diacetic acid (H_2dmedda). Sometimes we use L for these ligands.

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