Whether the type of behavior observed here will hold for the Rh_2^{4+} and Hg_2^{2+} aqua ions is of further interest. With Rh^{II}_2 the higher d-electron population and with Hg^{I}_2 the linear diaqua structure are features that could well lead to different behavior.

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Registry No. Mo_2^{4+}, 86711-98-0; NCS^-, 302-04-5; $HC_2O_4^-$, 920-52-5.

Supplementary Material Available: Listings of rate constants (Tables I-III) (3 pages). Ordering information is given on any current masthead page.

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Oxygen Atom Transfer Reactions. 4. Nitro/Nitrito Exchange in the Reaction of Nickel Dinitro Complexes with CO

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The oxidation of CO by $Ni(NO_2)_2L_2$ complexes produces CO_2 and $Ni(NO_2)(NO)L_2$ quantitatively. Reaction with $C^{18}O$ (99.6%) shows that the primary oxidation product is $C^{16}O^{18}O$ and that no ^{18}O is incorporated into the nickel complexes. In several cases (L = $P(CH_3)_2(C_6H_5)$, $P(C_6H_{11})_3$, and $P(C_4H_9)_3$), carbonyl intermediates were directly observed by using infrared and $^{31}P\{^1H\}$ NMR spectroscopy. Thus, these reactions are associative, forming $Ni(CO)(NO_2)_2L_2$ followed by an intramolecular transfer of an oxygen atom to CO and terminated by loss of CO_2. The solution stereochemistries of the reactants, intermediates, and products have also been investigated in the temperature range 190–330 K. The NO_2-containing complexes exhibited temperature-dependent $^{31}P\{^1H\}$ NMR signals indicative of exchange between $-NO_2$ and $-ONO$ isomers, but no exchange between $-NO$ and $-NO_2$ ligands was observed. Determination of the identity and solution stereochemistry of these species using $^{31}P\{^1H\}$ NMR spectra was aided by ^{15}N substitution (95%).

Introduction

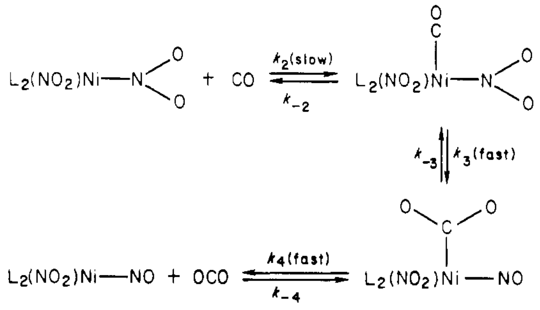
The oxidation of CO by $Ni(NO_2)_2L_2$ complexes of tertiary phosphines is well-known and has been reported previously:[1]

$$Ni(NO_2)_2L_2 + CO \rightarrow Ni(NO_2)(NO)L_2 + CO_2 \quad (1)$$

The observed rate law for the reaction of CO with $Ni(NO_2)_2$dppe and $Ni(NO_2)_2(PMe_3)_2$ is first order each in CO and nickel complex (k_2 values[1b,c] are 2.1×10^{-1} and 6.0×10^{-1} L mol^{-1} s^{-1}, respectively) and typical of square-planar complexes of nickel(II).[2] These observations are consistent with the previously proposed mechanism[1b-e] (Scheme I) in which the rate-determining step is formation of the monocarbonyl complex $Ni(CO)(NO_2)_2L_2$, followed by transfer of an oxygen atom to CO and terminated by loss of CO_2.

The only prior information about reactions 3 and 4 (Scheme I) was derived from the ^{18}O-labeling studies of Doughty et al.[1c] in which the observed distribution of ^{18}O in product CO_2 suggested that the nickel carbon dioxide complexes are sufficiently long-lived to undergo oxygen exchange with the NO_x ligands (reaction 3) before irreversibly losing CO_2 (reaction 4). The recent observation[1d] of equilibria between $-NO_2$ and $-ONO$ in these complexes also calls into question which isomer is responsible for oxygen atom transfer to CO. Moreover, direct attack of CO on the coordinated NO_2 ligand has recently been indicated for cobalt complexes[3] and has not been completely ruled out for the nickel complexes by the results of experiments thus far reported. It is the purpose of the present investigation to further elucidate the mechanism(s) of reaction 1 by examining the solution stereochemistries of reactants, products, and observable intermediates.

Scheme I. Proposed Mechanism for Oxidation of CO by $-NO_2$



Experimental Section

All operations were carried out under dry nitrogen unless otherwise specified. Solvents were of reagent grade and were purified by distillation immediately prior to use according to published procedure.[4] $Na^{15}NO_2$ (95% enriched) and $C^{18}O$ (99.63% enriched) were purchased from Prochem. Microanalyses were carried out by Huffman Laboratories, Wheatridge, CO, and Atlantic Microlabs, Atlanta, GA. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer Model 387 spectrometer. Electronic spectra were recorded on a Cary 14 UV-visible spectrophotometer.

Materials. $Ni(NO_2)_2L_2$ (L = PMe_3, PEt_3, PMe_2Ph, PPh_3, P-*n*-Bu_3, PCy_3, $^1/_2$ dppe, $^1/_2$ *cis*-vdpp, and $^1/_2$ dppp[5] were prepared by adding

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[2] (a) Cusmano, M.; Ricevuto, V. *J. Chem. Soc., Dalton Trans.* **1978**, 1682. (b) Murmann, R. K. *Inorg. Chem.* **1963**, *2*, 116. (c) Billo, E. J. *Ibid.* **1973**, *12*, 2783. (d) Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* **1961**, 2207. (e) Cattalini, L.; Martelli, M.; Rigo, P. *Inorg. Chim. Acta* **1967**, *1*, 149.

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[5] Me, Et, and Ph have their usual meaning, *n*-Bu is *n*-butyl, Cy is cyclohexyl, dppe is 1,2-bis(diphenylphosphino)ethane, *cis*-vdpp is *cis*-1,2-bis(diphenylphosphino)ethene, and dppp is 1,3-bis(diphenylphosphino)propane.

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Table I. Elemental Analyses for $Ni(NO_2)_2L_2$ Complexes

complex	color	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	% O calcd	% O found
$Ni(NO_2)_2(PMe_3)_2$	dark yellow	23.79	23.80	5.95	6.03	9.25	9.28		
$Ni(NO_2)_2(PEt_3)_2$	yellow-orange	37.24	37.24	7.76	7.75	7.24	7.82		
$Ni(NO_2)_2(PMe_2Ph)_2$	bright yellow	45.00	44.44	5.16	5.24	6.56	6.62		
$Ni(NO_2)_2(PMePh_2)_2$	bright yellow	56.66	56.78	4.72	4.85	5.08	5.19		
$Ni(NO_2)_2(PCy_3)_2$	yellow	60.79	60.31	9.29	9.48	3.94	3.70		
$Ni(NO_2)_2(P\text{-}n\text{-}Bu_3)_2$	yellow	51.90	51.88	9.80	10.26	5.04	4.89		
$Ni(NO_2)_2$dppe	orange	56.86	56.70	4.37	4.43	5.10	4.99	11.66	11.41
$Ni(NO_2)_2$(*cis*-vpp)	orange	57.07	56.90	4.02	4.22	5.12	4.96		
$Ni(NO_2)_2$dppp	orange	57.58	57.36	4.62	4.68	4.97	4.94		

Table II. Elemental Analyses for $Ni(NO_2)(NO)L_2$ Complexes

complex	color	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	% O calcd	% O found
$Ni(NO_2)(NO)(PMe_3)_2$	blue-black	25.12	25.05	6.32	6.66	9.76	9.91		
$Ni(NO_2)(NO)(PEt_3)_2$	blue-black	38.84	38.70	8.15	8.15	7.55	7.42		
$Ni(NO_2)(NO)(PMe_2Ph)_2$	blue-black	46.76	46.75	5.40	4.84	6.80	6.68		
$Ni(NO_2)(NO)$dppe	purple	58.57	58.37	4.50	4.58	5.26	5.06	9.01	9.59
$Ni(NO_2)(NO)$(*cis*-vpp)	purple	58.79	57.25	4.14	4.26	5.28	4.52		
$Ni(NO_2)(NO)$dppp	purple	59.27	59.10	4.76	4.78	5.12	5.06		

Table III. Room-Temperature $^{31}P\{^1H\}$ NMR Spectra of $Ni(NO_2)_2L_2$ and $Ni(NO_2)(NO)_2$ Complexes[a]

complex	δ[b]	peak width, Hz
$Ni(NO_2)_2L_2$ Complexes		
$Ni(NO_2)_2(PMe_3)_2$	−151.7	7
$Ni(NO_2)_2(PEt_3)_2$	−126.7	1
$Ni(NO_2)_2(PMe_2Ph)_2$	−146.3	7
$Ni(NO_2)_2(PMePh_2)_2$[c]	−137.0	11
$Ni(NO_2)_2(P\text{-}n\text{-}Bu_3)_2$	−133.7	2
$Ni(NO_2)_2(PCy_3)_2$	−125	2
$Ni(NO_2)_2$dppe	−87	120
$Ni(NO_2)_2$(*cis*-vpp)	−87	120
$Ni(NO_2)_2$dppp	−137	83
$Ni(NO_2)(NO)L_2$ Complexes		
$Ni(NO_2)(NO)(PMe_3)_2$	−138	
$Ni(NO_2)(NO)(PEt_3)_2$	−111	7
$Ni(NO_2)(NO)(PMe_2Ph)_2$	−131.3	6
$Ni(NO_2)(NO)(PCy_3)_2$	−91	4
$Ni(NO_2)(NO)$dppe	−88	7
$Ni(NO_2)(NO)$(*cis*-vpp)	−86	7
$Ni(NO_2)(NO)$dppp	−112.5	2.9

complex	coupling constants, Hz $^2J_{PP'}$ (cis)	$^2J_{PN'}$ (cis)	$^2J_{PN'}$ (trans)	$^2J_{NN'}$ (cis)
$Ni(^{15}NO_2)_2$dppe	47	−7	38	3
$Ni(^{14}NO_2)(O^{14}NO)$dppe	61			
$Ni(^{15}NO_2)(O^{15}NO)$dppe	63	7	not obsd	
$Ni(^{15}NO_2)Br(dppe)$	62	6	52	
$Ni(^{15}NO_2)Cl(dppe)$	65	~5	~52	
$Ni(^{15}NO_2)_2(PCy_3)_2$		8		
$Ni(^{15}NO_2)_2(PMe_2Ph)_2$		9		
$Ni(^{15}NO_2)_2(P\text{-}n\text{-}Bu_3)_2$		8		

[a] All spectra were obtained in $CDCl_3$. [b] Chemical shifts are relative to external TMP. [c] Spectra recorded after complex was in solution 10 min.

stoichiometric amounts of the appropriate phosphine ligand to methanolic solutions of "nickel nitrite"[6] according to published procedures (Table I).[1] Complexes enriched with ^{15}N were similarly prepared with $Na^{15}NO_2$ (95%). For L = $P\text{-}n\text{-}Bu_3$, the normal and enriched complexes were also prepared from $NiBr_2L_2$.[7] $Ni(NO)(NO_2)L_2$ complexes were prepared from the reaction of CO with $Ni(NO_2)_2L_2$ according to literature procedures (Table II).[1]

NMR Spectra. The $^{31}P\{^1H\}$ NMR spectra at 101.27 MHz were recorded on a Bruker Model WM 250 multinuclear spectrometer equipped with a variable-temperature probe and are referenced to external TMP. Typical spectra for complexes of unidentate phosphines were generated by using 500–1000 60° pulses with approximately 1.3-s acquisition times. The less soluble complexes of chelating phosphines required 3000–6000 pulses under similar conditions. Screw-cap 10-mm NMR tubes equipped with a serum-cap insert (Wilmad) were used. These tubes were sufficiently airtight for experiments with these air-sensitive compounds and also allowed for direct introduction of CO. Distilled and degassed deuterated and undeuterated solvents (Aldrich) were used in these experiments. For undeuterated solvents, a 5-mm coaxial tube of the pure deuterated solvent was added. No corrections for bulk magnetic susceptibility proved necessary. The ^{31}P chemical shifts are recorded in Table III.

Simulations. Static NMR simulations were done on the Aspect 2000 computer of the Bruker WM-250 spectrometer utilizing the PANIC 81 program.[8] Dynamic simulations were achieved with use of a local version of the DNMR 3 program.[9]

Detection of Intermediates. Saturated solutions of $Ni(NO_2)_2(PCy_3)_2$ in CH_2Cl_2 were stirred under CO (1 atm, 295 K) until a deep brown color developed (0.75 h). Solvent was evaporated under a stream of CO, and the infrared spectrum of the resulting brown powder was obtained (KBr pellet) (ν_{CO} = 1985, 2065 cm^{-1}). The progress of this reaction was also followed by $^{31}P\{^1H\}$ NMR spectroscopy. A solution of $Ni(NO_2)_2L_2$ (L = $P\text{-}n\text{-}Bu_3$, PCy_3, or PMe_2Ph) in toluene-d_8 was cooled in dry ice–acetone and CO added through the serum cap of the NMR tube. Spectra obtained at 220 K displayed the signals of reactants and products along with weak signals present only under reaction conditions. These weak signals appeared during the first 20% of the reaction and disappeared as the reaction proceeded to completion.

Isotopic Substitution. These experiments were carried out in a glass vacuum line equipped with a mercury diffusion pump and a Toepler pump for transfer of carbon monoxide. The ^{18}O-labeled CO (99.63%) was transferred to a gas bulb of known volume attached to a Schlenk flask containing $Ni(NO_2)_2(PMe_3)_2$ (0.1748 g, 0.577 mmol). With the connecting stopcock between bulb and flask closed, 20 mL of nitrogen-saturated benzene was added to the flask and the contents were subjected to three freeze–thaw cycles to ensure oxygen removal. The solution was then cooled with liquid nitrogen and the connecting stopcock opened. Four cycles of cooling to 77 K and rapid warming to 323 K accompanied by vigorous stirring were performed to ensure solution–gas mixing. The reaction was then allowed to proceed to approximately 93% completion (based on the rate constant,[1e] the $Ni(NO_2)_2(PMe_3)_2$ concentration, and the estimated $C^{18}O$ pressure) before it was quenched by freezing with a salt–ice slush at 263 K.

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Table IV. NO_2 Vibrational Frequencies of $Ni(NO_2)_2L_2$ Complexes[a]

complex	$\nu(NO_2)_{asym}$	$\nu(^{15}NO_2)_{asym}$	$\nu(NO_2)_{sym}$	$\nu(^{15}NO_2)_{sym}$	$\delta(NO_2)$	$\delta(^{15}NO_2)$	NO_2 rock	$^{15}NO_2$ rock
$Ni(NO_2)_2(PMe_3)_2$	1377	1353	1325	1305	820	812	619	604
$Ni(NO_2)_2(PEt_3)_2$	1374		1323		818		619	
$Ni(NO_2)_2(PMe_2Ph)_2$	1380	1355	1320	1300	820	812	617	601
$Ni(NO_2)_2(PMePh_2)_2$	1385	1362	1327	1306	820	815	620	605
$Ni(NO_2)_2(PCy_3)_2$	1390	1370	1318	1303	820	813		
$Ni(NO_2)_2(P\text{-}n\text{-}Bu_3)_2$	1385	1355	1320	1295	818	808	615	599
$Ni(NO_2)_2$dppe	1410	1380	1340	1315	819	811		
	1392	1365	1320	1297				
	1375	1350	1310	1288				
$Ni(NO_2)_2$(*cis*-vpp)	1410	1370	1335	1319	817	810		
	1400	1355	1322	1281				
	1381		1310					
$Ni(NO_2)_2$dppp	1400		1340		815			
	1390		1310					

[a] All frequencies are calibrated with use of the polystyrene bands at 1601 and 1028 cm^{-1} as standards. Spectra were determined in the solid state from KBr pellets.

Table V. Additional ^{15}N-Sensitive Vibrational Frequencies of $Ni(NO_2)_2L_2$ Complexes[a]

complex	^{14}N	^{15}N	^{14}N	^{15}N
$Ni(NO_2)_2(PMe_3)_2$	1155	1126		
$Ni(NO_2)_2(PEt_3)_2$	1149			
$Ni(NO_2)_2(P\text{-}n\text{-}Bu_3)_2$	1150	1119		
$Ni(NO_2)_2$dppe	1270	1240	1105	1075
$Ni(NO_2)_2$(*cis*-vpp)	1275	1245	1090	1065
$Ni(NO_2)_2$dppp	1270			

[a] All frequencies are calibrated by using the polystyrene bands at 1601 and 1028 cm^{-1} as standards. Spectra were determined in the solid state from KBr pellets.

To ensure removal of benzene, the gaseous products collected from the frozen solution were passed through three traps at 228 K (chlorobenzene slush) and trapped at 77 K. Any traces of unreacted carbon monoxide were then removed by pumping on the collected gas at 77 K for 10 min. The isolated carbon dioxide was analyzed by mass spectroscopy at the University of Arizona Analytical Center. The nickel-containing product was isolated by pumping the frozen solution to dryness and analyzed by infrared spectroscopy (KBr pellet) using a Perkin-Elmer Model 387 spectrometer.

Results

Synthesis and Characterization of Complexes. Each of the square-planar dinitro complexes of Ni(II), $Ni(NO_2)_2L_2$, were prepared from the reaction of methanolic solutions of nickel nitrite with stoichiometric amounts of the phosphine ligand (L = $^1/_2$ dppe, $^1/_2$ *cis*-vdpp, $^1/_2$ dppp, PMe_3, PEt_3, PMe_2Ph, PCy_3, $P\text{-}n\text{-}Bu_3$). These complexes were characterized by their elemental analyses and electronic and infrared spectra. The electronic spectra of these complexes are characterized by rapidly rising charge-transfer bands extending into the UV region with shoulders between 380 and 420 nm. Although many similar square-planar complexes of divalent nickel and their spectra are known, the ligand field transitions have not been identified with certainty.[10] Infrared spectra of these complexes exhibit frequencies characteristic of nitrogen-bound NO_2 ligands. Bands due to the antisymmetric and symmetric stretching modes of $Ni-NO_2$ groups were observed between 1374 and 1410 cm^{-1} (ν_{asym}) and 1310 and 1340 cm^{-1} (ν_{sym}) (Table IV). In free NO_2 these modes occur at 1450 and 1335 cm^{-1}, respectively.[11] The band assignments were verified by the 23–30-cm^{-1} shifts to lower frequencies observed in the ^{15}N-enriched compounds. Other $Ni-NO_2$ bands in the 810–820- and 615–620-cm^{-1} regions were identified by their isotopic shifts of 5–16 cm^{-1} and assigned to the $-NO_2$ bending and rocking modes, respectively. It also proved possible to distinguish the cis and trans isomers from their infrared spectra (cis isomers exhibit more NO_2 bands than do the trans isomers). The crystal structure of $Ni(NO_2)_2$dppe shows it to be monomeric with cis geometry.[12] Several dinitro complexes exhibit additional but weak absorption bands, which also shift upon ^{15}N substitution (Table V). Bands at 1090–1155 cm^{-1} are observed for the PMe_3, PEt_3, and $P\text{-}n\text{-}Bu_3$ complexes, while bands at 1240–1275 cm^{-1} are observed for the dppe, *cis*-vdpp, and dppp complexes. The bands between 1090 and 1155 cm^{-1} can be assigned to the O-bonded $-NO_2$ ligands while the bands between 1240 and 1275 cm^{-1} may be due to chelating NO_2 ligands by comparison with IR spectra of known compounds.[13] Thus, the IR spectra provide evidence for the presence of linkage isomers of these $NiNO_2$ complexes even in the solid state.

Table VI. Electronic Spectra for $Ni(NO_2)(NO)L_2$ Complexes

complex	abs band (ϵ)[a]
$Ni(NO_2)(NO)(PMe_3)_2$	571 (860)
	444 (835)
$Ni(NO_2)(NO)(PEt_3)_2$	584 (970)
	458 (1030)
$Ni(NO_2)(NO)(PMe_2Ph)_2$	576 (1020)
	450 (940)
$Ni(NO_2)(NO)$dppe	570 (690)
	460 (480)
$Ni(NO_2)(NO)$(*cis*-vpp)	590 (615)

[a] Positions of absorption bands are in nm. The extinction coefficients in parentheses have units of L mol^{-1} cm^{-1}. All spectra were determined in $CDCl_3$ with use of 1-cm glass cells.

Table VII. Infrared Data for $Ni(NO_2)(NO)L_2$ Complexes[a]

complex	NO	^{15}NO	additional non-phosphine bands
$Ni(NO_2)(NO)(PMe_3)_2$	1720		1270, 800
$Ni(NO_2)(NO)(PEt_3)_2$	1705		1365, 1330, 1310, 805
$Ni(NO_2)(NO)(PMe_2Ph)_2$	1725		1380, 1185, 805
$Ni(NO_2)(NO)(PCy_3)_2$	1725		
$Ni(NO_2)(NO)$dppe	1750	1715	1380, 1360, 1340, 1290, 1260, 1230, 815, 812
$Ni(NO_2)(NO)$(*cis*-vpp)	1745		
$Ni(NO_2)(NO)$dppp	1730		

[a] All frequencies are reported in cm^{-1} with the polystyrene bands at 1601 and 1028 cm^{-1} as standards. Spectra determined in the solid state with use of KBr pellets.

The $Ni(NO_2)(NO)L_2$ complexes were prepared in good yield from the reaction of $Ni(NO_2)_2L_2$ with CO. The nitrosyl

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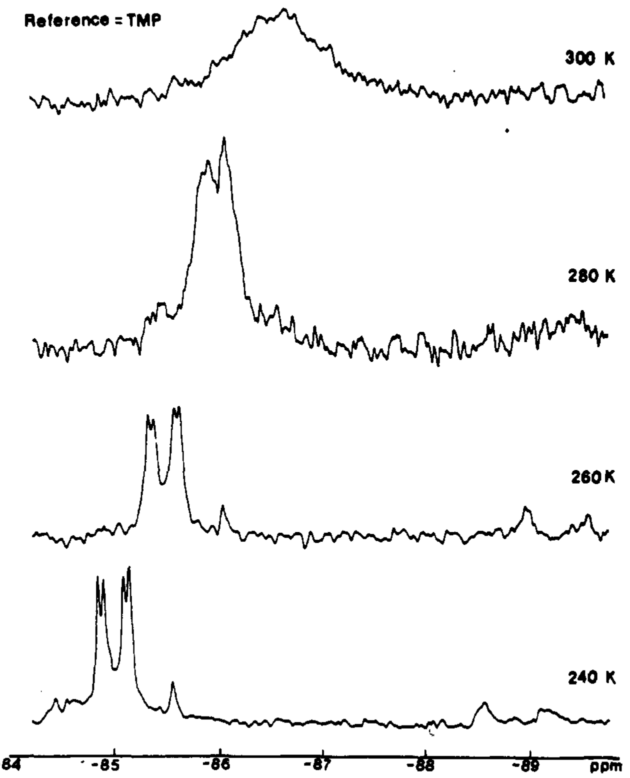


Figure 1. Temperature-dependent $^{31}P\{^1H\}$ NMR spectra of Ni($^{15}NO_2)_2$dppe in dichloromethane.

complexes are easily recognized by their dark blue to purple colors. Their electronic spectra consist of two bands with intensities between that expected for ligand field transitions and charge-transfer transitions (Table VI). The infrared spectra of nickel nitrosyl complexes are dominated by a strong ν(NO) between 1705 and 1750 cm^{-1} (Table VII). Bands characteristic of nitro and nitrito groups are also observed. For complexes with monodentate phosphine ligands, ν(NO) decreases with increasing ligand basicity. The possible relationship among NiNO bond angle, ν(NO), and the π-bonding model has been discussed elsewhere.[1f]

Since it is essential to have the maximum information about the molecular geometries of these complexes to understand their reactions with CO, their solutions have been studied by using $^{31}P\{^1H\}$ NMR spectroscopy. To differentiate between the various linkage isomers of the NO_2 ligand, the samples used for ^{31}P spectroscopy were enriched with ^{15}N (95%). At room temperature, the $^{31}P\{^1H\}$ spectra of *trans*-Ni($^{15}NO_2)_2L_2$ (L = P-*n*-Bu$_3$, PCy$_3$, and PMe$_2$Ph) exhibit sharp 1:2:1 triplets from coupling with two equivalent $^{15}NO_2$ ligands (Table III). Because the ^{15}N enrichment was only 95% in these samples, a weak doublet (intensity 1:13) with the same chemical shift as the triplet due to *trans*-Ni($^{15}NO_2$)($^{14}NO_2$)L_2 was also observed. No other ^{31}P signals attributable to isomeric –ONO complexes where observed in the spectra of these trans isomers.

The spectrum of *cis*-Ni($^{15}NO_2)_2$dppe is much more complicated. At 300 K, the broad signal observed is indicative of ligand exchange. As the temperature is lowered, this exchange process is slowed until the lower nonexchange limit is attained (Figure 1). At 220 K, the ^{15}N splitting is well resolved (Figure 2a). Simulation reproduces this spectrum faithfully using the following values of the coupling constants: $^2J_{PP}$ = 47 Hz, $^2J_{NN}$ = 3 Hz, $^2J_{PN}$(trans) = 38 Hz, $^2J_{PN}$(cis) = −7 Hz (Figure 2B). Several minor peaks are also present in the experimental spectrum, two at −88.5 ppm and at least two more centered around the main peak. The two weak peaks centered around the main peak correspond to the satellites expected for Ni($^{15}NO_2$)($^{14}NO_2$)dppe. This assignment has been confirmed by the spectrum obtained from a 50/50 mixture of Ni($^{15}NO_2)_2$dppe and Ni($^{14}NO_2)_2$dppe, where these lines are enhanced by the statistical amount.

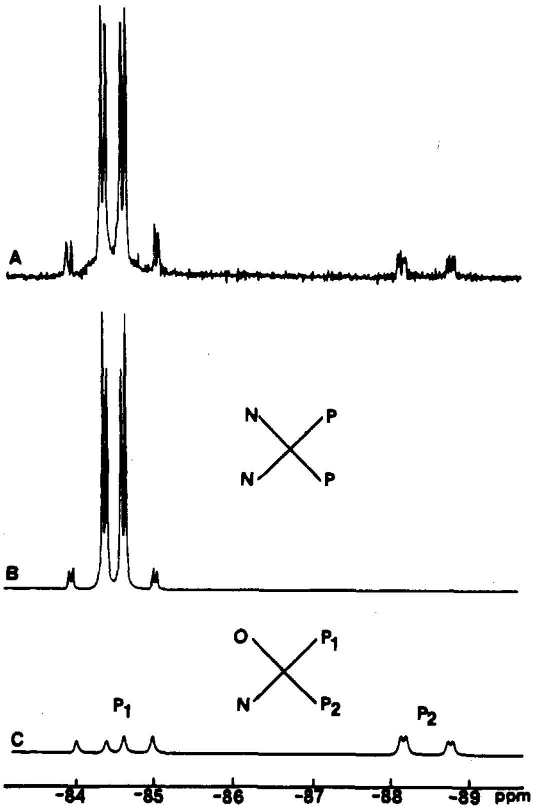


Figure 2. (A) $^{31}P\{^1H\}$ NMR spectrum of Ni($^{15}NO_2)_2$dppe at 220 K in dichloromethane. (B) Simulated ^{31}P NMR spectrum of Ni($^{15}NO_2$)dppe. (C) Simulated ^{31}P NMR spectrum of Ni($^{15}NO_2$)($O^{15}NO$)dppe.

The two additional peaks at −88.5 ppm are due to another chemical species with an AA′X pattern. The concentration of this species is independent of the method of synthesis and of ^{15}N enrichment. The simulated spectrum of Ni(ONO)(NO$_2$)dppe shown in Figure 2C, is a typical AA′X pattern. The ^{31}P spectrum of this species is also similar to that observed for Ni(NO$_2$)Br(dppe) and Ni(NO$_2$)Cl(dppe) (Table III). The temperature dependence of the ^{31}P NMR spectrum of Ni(NO$_2)_2$dppe was simulated by using a local version[9] of DNMR 3 and yielded approximate rate constants for the –NO$_2$/–ONO interconversion of 55–65 s^{-1} at coalescence. These rate studies are not yet complete, and consequently, the rate constants should be considered to have only qualitative significance. This evidence for –NO$_2$/–ONO interconversion in solution obtained from the ^{31}P spectra is also substantiated by the observation of weak nitrito bands in the infrared spectrum of Ni(NO$_2)_2$dppe (Table V).

Less detailed information is available regarding the disposition of the NO$_2$ ligand in Ni(NO)(NO$_2)L_2$ complexes. However, the $^{31}P\{^1H\}$ NMR spectra of the tetrahedral Ni(^{15}NO)($^{15}NO_2)L_2$ complexes each exhibit a primary resonance consisting of a doublet of doublets and a less intense doublet consistent with the presence of the Ni(^{15}NO)($O^{15}NO)L_2$ isomer. These tetrahedral Ni(NO)(NO$_2)L_2$ complexes are also fluxional as evidenced by the temperature dependence of the NMR spectra of Ni(^{15}NO)($^{15}NO_2$)dpp and Ni(^{15}NO)($^{15}NO_2$)(PMe$_3)_2$ (Figure 3).

Reactions of Ni(NO$_2)_2L_2$ with C^{18}O. The reaction of Ni(NO$_2)_2$(PMe$_3)_2$ with C^{18}O (99.63% enriched) yielded useful mechanistic information. Stoichiometric amounts of these two compounds were allowed to react for 5.5 h, and the nickel product was examined by infrared spectroscopy. No evidence

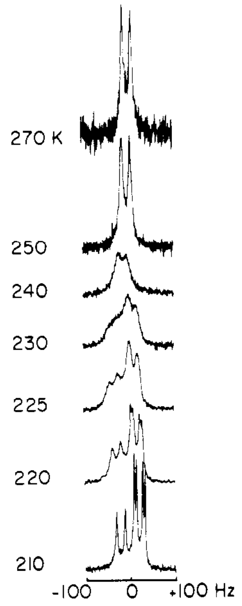


Figure 3. Temperature-dependent $^{31}P\{^1H\}$ NMR spectra of Ni($^{15}NO_2$)(^{15}NO)(PMe_3)$_2$ in dichloromethane.

of ^{18}O incorporation into the nitrosyl group was found by comparison with the complex isolated from the reaction with $C^{16}O$ under identical experimental conditions. The carbon dioxide evolved was collected at 77 K, fractionated, and identified by mass spectroscopy. The predominant species was $C^{16}O^{18}O$ (74%). Since no ^{18}O was incorporated into the nickel nitrosyl product, a secondary process is responsible for the observed ^{18}O–^{16}O scrambling (26%) in the produce CO_2. These results agree with those reported by Doughty et al.,[1c] who found incorporation of ^{18}O in the carbon dioxide evolved from the reaction of $C^{16}O$ with a sample of $Ni(NO_2)_2(PEt_3)_2$ 1% enriched with ^{18}O. However, Doughty et al. concluded from their gas analyses that ^{18}O was incorporated into the Ni–NO_x complexes but did not analyze them for ^{18}O. The high enrichment of ^{18}O, which was used in the present experiments, shows that no appreciable ^{18}O is incorporated into the nickel complexes, and thus the observed reaction with ^{18}O-labeled CO can be summarized as

$$Ni(NO_2)_2(PMe_3)_2 + C^{18}O \rightarrow Ni(N^{16}O_2)(N^{16}O)(PMe_3) + C^{16}O^{18}O \quad (5)$$

In addition to these isotopic studies, carbonyl intermediates have been observed directly with infrared and ^{31}P NMR spectroscopy (Figure 4). When the reaction between CO and $Ni(NO_2)_2(PCy_3)_2$ was allowed to proceed for short periods of time, an impure carbonyl intermediate was observed (ν(CO) = 1985, 2065 cm^{-1}; $^{31}P\{^1H\}$ NMR 100.9 ppm; Figure 4). Although other carbonyl intermediates could not be isolated, they were observed in the ^{31}P NMR spectra.

Discussion and Conclusions

This series of *cis*- and *trans*-$Ni(NO_2)_2L_2$ complexes consists of planar, four-coordinate, diamagnetic monomers. The NO_2 ligands are primarily N bonded, although they do undergo linkage isomerism in solution. Except for the PCy_3 and P-*n*-Bu_3 derivatives, the NO_2 isomers interconvert rapidly on the ^{31}P NMR time scale at room temperature. This interconversion between $-NO_2$ and –ONO is effectively quenched at 200–220 K. In spite of the ease of interconversion of the $-NO_2$ and –ONO isomers, the $-NO_2$ isomer predominates for all L at all temperatures that were investigated.

Each complex reacts quantitatively with CO under ambient conditions of temperature and pressure ot yield the nitrosyl complexes, $Ni(NO_2)(NO)L_2$. The molecular structures of several of these tetrahedral diamagnetic nitrosyl complexes have been reported elsewhere.[14] The $-NO_2$ ligands of these nickel nitrosyl complexes also undergo linkage isomerism as evidenced by their ^{31}P NMR spectra.

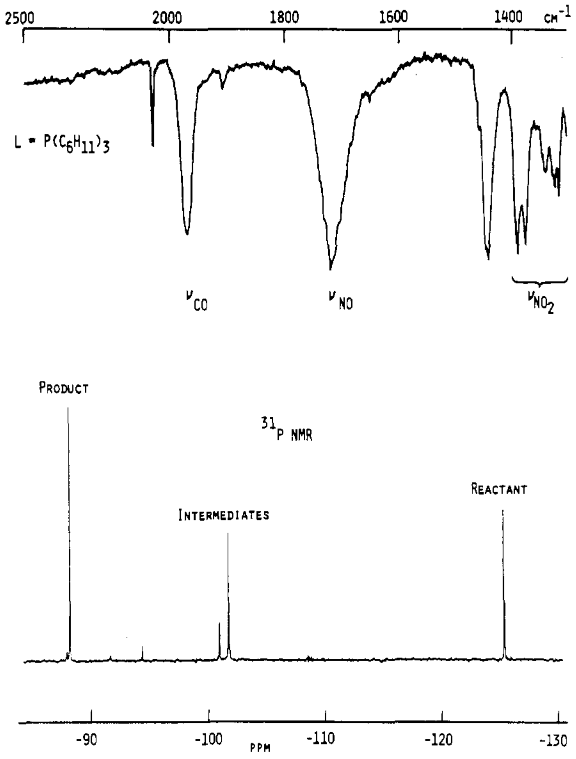
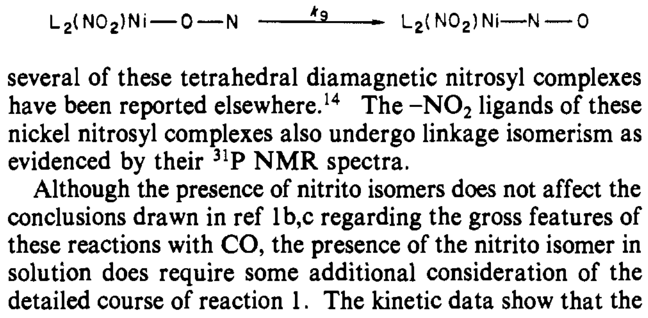


Figure 4. Infrared spectrum (upper curve) and $^{31}P\{^1H\}$ NMR spectrum (lower curve) of the impure carbonyl intermediates Ni(CO)(NO_2)$_2$(PCy_3)$_2$, obtained from the reaction of CO with $Ni(NO_2)_2$(PCy_3)$_2$.

Scheme II. Proposed Mechanism for Oxidation of CO by -ONO



Although the presence of nitrito isomers does not affect the conclusions drawn in ref 1b,c regarding the gross features of these reactions with CO, the presence of the nitrito isomer in solution does require some additional consideration of the detailed course of reaction 1. The kinetic data show that the reaction is associative since the rates depend upon the concentrations of both CO and the nickel complex.[1b] Moreover, CO intermediates have been observed by ^{31}P NMR spectroscopy, and impure compounds containing both CO and $-NO_2$ lingands have been isolated and characterized by infrared spectroscopy. Nevertheless, the rapid iterconversion of the NO_2 linkage isomers does require the additional mechanistic considerations summarized in Scheme II.

In Scheme II, a rapid preequilibrium between both forms of coordinated NO*2* precedes reaction of the nickel complex with CO. The attack of carbon monoxide and subsequent

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[14] Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

oxygen atom transfer may then occur via either a nitrito (Scheme II) or a nitro isomer (Scheme I). The oxygen atom transfer step would appear to be facilitated by the larger ring formed by a nitrito ligand in the transition state in Scheme II, while thermodynamics would favor the direct formation of the N-bonded isomer of the nitrosyl ligand in Scheme I. At the present time, there is insufficient experimental evidence available to distinguish between these two possible reaction routes. In spite of the uncertainty regarding which of the two NO_2 linkage isomers is responsible for the oxygen atom transfer to CO, it is clear that the reaction proceeds via the formation of a five-coordinate carbonyl intermediate. Moreover, once the oxygen atom is transferred from the NO_2 ligand to the CO ligand, CO_2 is lost *before* it can exchange with the resulting NO and NO_2 ligands. CO_2 and $Ni(NO_2)(NO)L_2$ are produced quantitatively, but at rates that are dependent upon L. Our studies also show that *^{18}O is not incorporated into the nickel products*, even though some scrambling of the ^{18}O and ^{16}O isotopes in CO_2 was observed.

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Registry No. $Ni(NO_2)_2(PMe_3)_2$, 20663-81-4; $Ni(NO_2)_2(PEt_3)_2$, 86941-01-7; $Ni(NO_2)_2(PMe_2Ph)_2$, 25456-46-6; $Ni(NO_2)_2(PMePh_2)_2$, 86886-05-7; $Ni(NO_2)_2(PCy_3)_2$, 86886-06-8; $Ni(NO_2)_2(P\text{-}n\text{-}Bu_3)_2$, 24510-66-5; $Ni(NO_2)_2$dppe, 71604-08-5; $Ni(NO_2)_2$(*cis*-vpp), 86886-07-9; $Ni(NO_2)_2$dppp, 86886-08-0; $Ni(NO_2)(NO)(PMe_3)_2$, 79499-32-4; $Ni(NO_2)(NO)(PEt_3)_2$, 86886-09-1; $Ni(NO_2)(NO)(PMe_2Ph)_2$, 86886-10-4; $Ni(NO_2)(NO)$dppe, 86886-11-5; $Ni(NO_2)(NO)$(*cis*-vpp), 86886-12-6; $Ni(NO_2)(NO)$dppp, 86886-13-7; $Ni(NO_2)(NO)(PCy_3)_2$, 86886-14-8; CO, 630-08-0.

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Copper(II) Chloride Complex Equilibrium Constants

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The solubility of recrystallized copper iodate hydrate was determined, by using high-accuracy controlled-potential coulometry, in solutions of copper perchlorate and in solutions of sodium chloride, all at ionic strength 5 with sodium perchlorate as the inert electrolyte. The association constant for the $CuIO_3^+$ species and the solubility product for copper iodate were determined at 25 and 35 °C. From the effects of chloride ion on the solubility at 25 °C, the four successive β values for copper chloride complexes were determined and compared with results of spectrophotometric measurements. Revised enthalpy changes for the complexation steps were calculated.

The thermodynamic characterization of the reactions that occur when chloride ion is added to a copper(II) perchlorate solution is an inorganic chemistry problem of long standing. The color changes gradually from blue to green with increased absorption both in the ultraviolet (250–275 nm) and at the high end of the visible spectrum (700–800 nm). Absorption spectra of the solutions have been repeatedly examined with the goal of determining the equilibrium constants for the formation of the successive complexes

$$M + jL = ML_j$$

where $j = 1$–4 and M and L represent the tetraaquocopper(II) ion and the chloride ion, respectively. The system may be described in terms of β values, which are overall equilibrium constants $\beta_j = [ML_j]/[M][L]^j$, or in terms of the individual equilibrium constants for each step $Q_j = [ML_j]/[ML_{j-1}][L]$.

A recent paper by Arnek et al.[1] presents a calorimetric study of the system and includes a useful summary of previous equilibrium research under a variety of conditions of ionic strength.

Three studies of this system have been reported for an ionic strength of 5, permitting the high chloride concentrations needed for appreciable formation of the higher complexes. Schwing-Weill[2,3] obtained a comprehensive set of ultraviolet–visible spectra for a large number of copper–chloride mixtures and applied least-squares analysis to estimate values for the equilibrium constants and for the molar absorptivities. Bjerrum and Skibsted[4] suggested reinterpretation of Schwing-Weill's data on the basis of data in very concentrated chloride media. Ashurst and Hancock[5] used their own data under selected conditions to obtain another set of equilibrium constants. The lack of agreement in these studies gives support to the closing paragraph of Bjerrum and Skibsted:

"The conclusion of this paper is that attempts to obtain quantitative results in studies of consecutive weak complex formation in solution necessitate the use of many approximations, and studies of such systems can therefore be expected to give only semiquantitative results."

Given the inherent problem of the spectrophotometric approach to this system, namely that the data must be treated with both the equilibrium constants and the molar absorptivities as unknown parameters, it seemed very desirable to study the copper–chloride system by using a method completely independent of spectrophotometry, i.e. by measuring the effect of varying chloride concentration on the solubility of copper(II) iodate. Accurate equilibrium constants are also required for the interpretation of the calorimetric study,[1] which also was performed at ionic strength 5.

The theoretical and computational basis for the use of solubility of a metal iodate as a chemical probe for finding metal–ligand complex formation constants has been described for an analogous study of cadmium bromide complexes.[6] The

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