Nitro and Nitrato Complexes of Cyclopentadienyl(*N*,*N*-dialkyldithiocarbamato)cobalt(III). Preparation and Use as Oxidants

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The preparation of a series of cyclopentadienyl(*N*,*N*-dialkyldithiocarbamato)cobalt(III) complexes, $CpCo(S_2CNR_2)X$ (R = CH_3, C_2H_5; X = I, NO_2, NO_3) and $[CpCo(S_2CN(CH_3)_2)L]X$ (L = Ph_3P, X = I, BF_4; L = CH_3CN, X = BF_4), is described. Mixtures of $CpCo(S_2CN(CH_3)_2)NO_2$ and $BF_3{\cdot}Et_2O$ were found to oxidize benzyl alcohol to benzaldehyde. The reaction is stoichiometric in the absence of oxygen. Benzyl alcohol is also oxidized by mixtures of $CpCo(S_2CN(CH_3)_2)NO_3$, $PPNNO_2$, and $PPNNO_3$ (PPN = $(Ph_3P)_2N$) with $BF_3{\cdot}Et_2O$. The oxidations by the nitrate species are catalytic in the presence of oxygen. The detailed results rule out mechanisms for the metal nitro complex reactions that involve metal-bound nitrogen oxide ester intermediates. A mechanism in which NO_2^- reacts with BF_3 to give the actual oxidant is proposed.

Introduction

Certain transition-metal nitro complexes undergo redox reactions with oxidizable organic substrates. The reactions are known or thought to occur via metal-bound nitrogen oxide ester intermediates, and the nitrogen oxide ligands are thought to remain coordinated to metal throughout the processes. The reactions are stoichiometric in the absence of oxygen and catalytic via the MNO_2/MNO redox couple in its presence. As the examples, $(CH_3CN)_2PdXNO_2$ (X = Cl, NO_2) oxidize olefins to carbonyl[1] or epoxide[2] products and $LCo(py)NO_2$ (L = tetraphenylporphyrin, *o*-phenylenediamine bis(salicylimine); py = pyridine) oxidize primary and secondary alcohols to carbonyl products[3] and olefins to carbonyl[4] or epoxide[5] products.

These catalytic reactions are attractive for synthetic purposes because they can use air as the ultimate oxidant under mild conditions. Unlike most oxidations with molecular oxygen these seem not to involve free radical chain reactions. This suggests that the processes could have high selectivity. On the basis of these considerations, we have initiated a search for other useful catalyst systems. Several considerations led us to focus our attention on the $CpCo^{III}$ (Cp = η^5-cyclopentadienyl) moeity. One of the most rigid requirements for the complexes involved is that they not be decomposed by oxygen. $CpCo^{III}$ is an excellent choice in this regard. *N*,*N*-Dialkyldithiocarbamate (R_2NCS_2) auxiliary ligands were chosen for the same property. Moreover, both Cp and R_2NCS_2 were expected to be stable with respect to substitution.

A series of cyclopentadienyl(*N*,*N*-dialkyldithiocarbamato)cobalt(III) complexes ($CpCo(S_2CNR_2)X$) was prepared. The synthesis and subsequent reactions of these complexes demonstrate that displacement of X is facile. The complexes with X = NO_2 and NO_3 oxidize benzyl alcohol to benzyaldehyde in the presence of $BF_3{\cdot}Et_2O$. Contrary to expectations, displacement of X seems to dominate these reactions as well.

Experimental Section

General Information. The preparative reactions were performed in air at room temperature unless otherwise noted. $CpCo(CO)I_2$ was prepared by iodine oxidation of $CpCo(CO)_2$ in diethyl ether.[6] PPNX (X = NO_2, NO_3, BF_4) were prepared from PPNCl and NaX by a general literature procedure.[7] Silica gel was used for thin-layer and column chromatography. Infrared and ^1H NMR spectra were recorded on Perkin-Elmer PE297 and Varian CFT-20 instruments, respectively. Melting points were determined by using a Laboratory Devices Mel-Temp instrument and are uncorrected. Elemental analyses were obtained from M-H-W Laboratories.

The solvents and reagents used in the benzyl alcohol oxidation reactions were purified by literature methods[8] and stored under argon. Gas chromatographic analyses were done by using a Hewlett-Packard HP5840A instrument with a 3.65 m × 0.32 cm nickel column packed with 6% Carbowax 20M on 80/100 mesh Chromosorb 750. Products were identified by coinjection with authentic materials, and absolute yields were obtained by using *n*-tetradecane as internal standard. Benzaldehyde was further identified by GC/MS.

$CpCo(S_2CN(CH_3)_2)I$ (1a). A solution of sodium *N*,*N*-dimethyldithiocarbamate dihydrate (1.79 g, 10.0 mmol) in acetone (70 mL) was added to a solution of $CpCo(CO)I_2$ (4.07 g, 10.0 mmol) in acetone (40 mL), resulting in an immediate color change from purple to green and evolution of carbon monoxide (identified by gas-phase infrared). After 30 min the solvent was removed on a rotary evaporator. Dichloromethane (175 mL) was added to the residue, and the resulting suspension was dried over magnesium sulfate. Filtration and evaporation of the solvent on a rotary evaporator gave **1a** (3.40 g, 92%). Purification by column chromatography (heptane/dichloromethane) gave dark green crystals; TLC, heptane/dichloromethane, 1:9, R_f 0.13. Anal. Calcd for $C_8H_{11}CoINS_2$: C, 25.89; H, 2.99; N, 3.77. Found: C, 25.79; H, 2.97; N, 3.60.

$CpCo(S_2CN(C_2H_5)_2)I$ (2a). Prepared as described above using sodium *N*,*N*-diethyldithiocarbamate trihydrate (0.61 g, 2.7 mmol) and $CpCo(CO)I_2$ (1.0 g, 2.5 mmol), crude **2a** (1.0 g, 100%) was purified twice by column chromatography (heptane/dichloromethane) and recrystallized by slow evaporation of a heptane/dichloromethane solution to give dark green crystals; TLC, heptane/dichloromethane, 1:9, R_f 0.24. Anal. Calcd for $C_{10}H_{15}CoINS_2$: C, 30.09; H, 3.79; N, 3.51. Found: C, 30.11; H, 4.00; N, 3.52.

$CpCo(S_2CN(CH_3)_2)NO_2$ (1b). A solution of sodium nitrite (0.35 g, 5.0 mmol) in water (5 mL) was added to a solution of **1a** (0.37 g, 1.0 mmol) in acetonitrile (5 mL) resulting in a color change from green to purple over a period of ~5 min. After 1 h, the reaction mixture was extracted with dichloromethane (3 × 10 mL) and the combined extracts were washed with water (3 × 10 mL) and saturated aqueous sodium chloride (1 × 10 mL). After the

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[1] Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894.

[2] Andrews, M. A.; Cheng, C.-W. F. *J. Am. Chem. Soc.* **1982**, *104*, 4268.

[3] Tovrog, B. S.; Diamond, S. E.; Mares, F.; Szalkiewicz, A. *J. Am. Chem. Soc.* 1981, *103*, 3522.

[4] Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616.

[5] Diamond, S. E.; Mares, F.; Szalkiewicz, A.; Muccigrosso, D. A.; Solar, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4266.

[6] King, R. B. *Inorg. Chem.* **1966**, *5*, 82.

[7] Martinsen, A.; Songstad, J. *Acta Chem. Scand., Part A* **1977**, *31A*, 645.

[8] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 1st ed.; Pergamon Press: New York, 1966.

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solution was dried over magnesium sulfate, the solvent was evaporated on a rotary evaporator to give **1b** (0.26 g, 90%). Purification by column chromatography (dichloromethane/acetone) gave dark purple crystals; TLC, dichloromethane/acetone, 4:1, R_f 0.40. Anal. Calcd for $C_8H_{11}CoN_2O_2S_2$: C, 33.11; H, 3.82; N, 9.65. Found: C, 33.09; H, 3.86; N, 9.52.

$CpCo(S_2CN(C_2H_5)_2)NO_2$ (2b). Prepared as described above using sodium nitrite (0.17 g, 2.5 mmol) and **2a** (0.20 g, 0.50 mmol), the crude product was purified by column chromatography (dichloromethane/acetone) to give **2b** (0.12 g, 75%) as dark purple crystals; TLC, dichloromethane/acetone, 4:1, R_f 0.47. Anal. Calcd for $C_{10}H_{15}CoN_2O_2S_2$: C, 37.74; H, 4.75; N, 8.80. Found: C, 37.64; H, 4.76; N, 8.61.

$CpCo(S_2CN(CH_3)_2)NO_3$ (1c). A solution of silver nitrate (0.37 g, 2.2 mmol) in acetonitrile (10 mL) was added to a solution of **1a** (0.74 g, 2.0 mmol) in acetonitrile (10 mL). A color change from green to purple and formation of a white solid occurred immediately. After 1.5 h, the reaction mixture was filtered by using diatomaceous earth and the solvent was evaporated from the filtrate on a rotary evaporator to give **1c** (0.54 g, 88%). Purification by column chromatography (dichloromethane/acetone) gave dark blue crystals; TLC, dichloromethane/acetone, 1:9, R_f 0.11. Anal. Calcd for $C_8H_{11}CoN_2O_3S_2$: C, 31.38; H, 3.62; N, 9.15. Found: C, 31.12; N, 3.69; N, 9.39.

$CpCo(S_2CN(C_2H_5)_2)NO_3$ (2c). Prepared as described above using silver nitrate (0.19 g, 1.1 mmol) and **2a** (0.40 g, 1.0 mmol), crude **2c** (0.27 g, 80%) was purified by column chromatography (dichloromethane/acetone, repeated once), and recrystallized by slow evaporation of a heptane/acetone solution to give dark blue crystals; TLC, dichloromethane/acetone, 1:9, R_f 0.23. Anal. Calcd for $C_{10}H_{15}CoN_2O_3S_2$: C, 35.93; H, 4.52; N, 8.38. Found: C, 36.01; H, 4.46; N, 8.44.

$[CpCo(S_2CN(CH_3)_2)(Ph_3P)]I$ (3a). A solution of triphenylphosphine (0.39 g, 1.5 mmol) and **1a** (0.37 g, 1.0 mmol) in dichloromethane (25 mL) was heated under reflux for 15 min. The dark red solution was cooled, concentrated to a volume of ~5 mL, and added to ethyl ether (50 mL). Filtration gave **3a** (0.56 g, 88%). Purification by column chromatography (dichloromethane/methanol) gave red crystals; TLC, dichloromethane/methanol, 19:1, R_f 0.24.

$[CpCo(S_2CN(CH_3)_2)(Ph_3P)]NO_3$ (3c). Prepared as described above using triphenylphosphine (0.11 g, 0.43 mmol) and **1c** (0.09 g, 0.29 mmol) in 1,2-dichloroethane (10 mL) as solvent, crude **3c** (0.15 g, 90%) was purified by column chromatography (dichloromethane/methanol) to give red crystals; TLC, dichloromethane/methanol, 19:1, R_f 0.10.

$[CpCo(S_2CN(CH_3)_2)(Ph_3P)]BF_4$ (3d). A solution of silver tetrafluoroborate (0.80 g, 0.40 mmol) in acetonitrile (5 mL) was added to a solution of **3a** (0.20 g, 0.32 mmol) in acetonitrile (5 mL). A white solid formed immediately. After 1 h, the reaction mixture was filtered by using diatomaceous earth and the solvent was evaporated on a rotary evaporator. The crude product was purified by column chromatography (dichlormethane/methanol) to give **3d** (0.18 g, 95%) as dark red crystals; TLC, dichloromethane/methanol, 19:1, R_f 0.31. Anal. Calcd for $C_{26}H_{26}BCoF_4NPS_2$: C, 52.63; H, 4.42; N, 2.36. Found: C, 52.83; H, 4.58; N, 2.36.

$[CpCo(S_2CN(CH_3)_2)(CH_3CN)]BF_4$ (4d). Prepared as described above using silver tetrafluoroborate (0.43 g, 2.2 mmol) and **1a** (0.74 g, 2.0 mmol), the crude product was purified by column chromatography (dichloromethane/acetonitrile) to give **4d** (0.66 g, 89%) as dark purple crystals; TLC, dichloromethane/methanol, 19:1, R_f 0.23.

Oxidation of Benzyl Alcohol. Stoichiometric Reactions. The reactions were performed in the absence of oxygen by using standard Schlenk techniques. The oxidant (0.10 mmol) was placed in a 15-mL three-neck round-bottom flask fitted with a septum, a gas inlet, and a gas infrared cell. *n*-Tetradecane (0.15–0.20 mmol), benzyl alcohol (2.5 mmol), and solvent (1,2-dichloroethane or nitrobenzene, 1.75 mL) were added. After ~1 min was allowed for the solid to dissolve, $BF_3 \cdot Et_2O$ was added and the reaction flask was immersed in an oil bath held at 60–65 °C.

The reaction mixtures were analyzed by gas chromatography after 10 and 45 min. Benzaldehyde and benzyl ether were observed in all reactions. After 45 min, the oil bath was removed and the colorless gases above the cooled reaction mixtures were sampled and analyzed. The infrared spectra all included bands for nitrous oxide (2240, 2220 cm^{-1}), nitric oxide (1880 cm^{-1}), and volatile organics (ethyl ether, solvent).

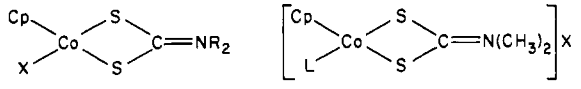
A dark purple solid was isolated from the reactions with **1b** and **1c** by addition of ethyl ether (25 mL) to the final mixtures. The infrared spectra included bands consistent with cyclopentadienyl (3100, 1420, 840, 825 cm^{-1}) and *N,N*-dimethyldithiocarbamato ligands (1550, 1400, 1250 cm^{-1}) and tetrafluoroborate (1050 cm^{-1}). The product reacted with triphenylphosphine, in nitrobenzene solution or as a suspension in 1,2-dichloroethane, to give **3d** in 70–80% purified yield.

The oxidation reactions with $PPNNO_2$ and $PPNNO_3$ gave $PPNBF_4$ in 80–90% isolated yield. Melting points of typical samples were in the range 235–240 °C.[9]

Catalytic Reactions. The reactions were performed essentially as described above by using a 10-mL two-neck round-bottom flask fitted with a septum and a reservoir of dry oxygen. The solvent was saturated with oxygen before use. The reaction mixtures were analyzed by gas chromatography after 10, 60, and 120 min. Benzaldehyde and benzyl ether were observed in all reactions.

Results and Discussion

Preparation and Characterization of Cobalt Complexes. A series of cyclopentadienyl(*N,N*-dialkyldithiocarbamato)cobalt(III) complexes was prepared. The synthesis of the iodo complexes **1a** and **2a** by displacement reactions involving $CpCo(CO)I_2$ was expected on the basis of literature precendent. Reactions of $CpCo(CO)I_2$ with neutral, monodentate species to give $CpCoLI_2$ (L = triphenylphosphine, pyridine)[6] and neutral, bidentate species to give $[CpCoL'I]I$ (L′ = 2,2′-bipyridine,[6] 1,2-bis(diphenylphosphino)ethane,[10] *o*-phenylenediamine[11]) are known. The reactions with sodium dialkyldithiocarbamates to give **1a** and **2a** extend the series to include anionic, bidentate nucleophiles.[12]



1a–c, R = CH_3
2a–c, R = C_2H_5

3a–d, L = Ph_3P
4d, L = CH_3CN

a, X = I; b, X = NO_2; c, X = NO_3; d, X = BF_4

The new iodo complexes give the expected spectroscopic data (Table I). The cyclopentadienyl ligands give rise to the usual infrared bands[13] and to singlets at ~5.20 ppm in the ^1H NMR. The infrared band at 1530 cm^{-1} is consistent with chelated dimethyldithiocarbamate,[14] and the singlet for the methyl protons is at 3.20 ppm in the ^1H NMR. The diethyldithiocarbamate ligand of **2a** shows a band at 1505 cm^{-1} in the infrared and an ABX_3 pattern in the ^1H NMR. The methylene protons of the ethyl groups are magnetically nonequivalent due to restricted rotation about the C=N bond, and an apparent difference in chemical shift of 2–4 Hz is observed.

Complex **1a** reacts with triphenylphosphine to give the cationic complex **3a**. The ^1H NMR multiplet for the aromatic phosphine protons of **3a** is shifted ~0.30 ppm downfield of that for the free ligand, reflecting the extent to which electron density is donated to metal. The singlet for the carbamate methyl protons is shifted ~0.45 ppm

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[9] Authentic $PPNBF_4$, prepared from PPNCl and $NaBF_4$ and recrystallized from acetone/diethyl ether, melted at 231–232 °C.

[10] Landon, S. J.; Brill, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6571.

[11] Heck, R. F. *Inorg. Chem.* **1968**, *7*, 1513.

[12] An analogous complex, CpCo(π-allyl)I, is obtained in low yield by the reaction of $CpCo(CO)_2$ and allyl iodide. Heck, R. F. *J. Org. Chem.* **1963**, *28*, 604.

[13] Brunner, H.; Wachsmann, H. *J. Organomet. Chem.* **1968**, *15*, 409.

[14] Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233.

Table I. Infrared and ^1H NMR Data

compd	infrared,[a] cm^{-1}	solv	^1H NMR chem shift[d]		
			Cp	R	L
1a	3100 vw, 1530 s, 1445 w, 1425 w, 1395 s, 1250 m, 1150 m, 1135 sh, 1055 w, 1010 w, 980 m, 860 w, 840 m, 825 m	$CDCl_3$	5.22 s	3.21 s	
		CD_3CN	5.21 s	3.16 s	
2a	3100 vw, 2970 w, 2920 w, 1505 s, 1450 sh, 1435 s, 1410 m, 1375 w, 1365 sh, 1355 m, 1280 s, 1205 m, 1145 m, 1070 m, 1005 w, 990 m, 910 w, 845 m, 825 sh, 815 s	$CDCl_3$	5.21 s	3.58,[e] 1.20 t	
		CD_3CN	5.22 s	3.55 q, 1.20 t	
3a	3095 vw, 3030 w, 1550 s, 1465 m, 1430 s, 1415 sh, 1400 s, 1310 w, 1250 m, 1160 m, 1095 m, 1085 m, 1010 w, 995 m, 980 w, 895 w, 870 w, 845 m, 825 w, 750 s, 745 sh, 705 sh, 695 s	$CDCl_3$	5.38 s	2.75 s	7.55 m
1b	$\nu(NO_2)$ 1372 s, 1312 s, 815 s	$CDCl_3$	5.30 s	3.22 s	
	$\nu(C{=}N)$ 1542 s	CD_3CN	5.30 s	3.17 s	
2b	$\nu(NO_2)$ 1380 s, 1315 s, 818 sh	$CDCl_3$	5.30 s	3.60,[e] 1.25 t	
	$\nu(C{=}N)$ 1512 s				
1c	$\nu(NO_3)$ 1468 s, 1380 vs,[b] 1270 s, 982 sh, 800 s	$CDCl_3$	5.41 s	3.20 s	
	$\nu(C{=}N)$ 1550 s	CD_3CN	5.53 s	3.19 s	
2c	$\nu(NO_3)$ 1480 s, 1360 vs,[b] 1270 s, 992 s, 800 m	$CDCl_3$	5.41 s	3.64,[e] 1.20 t	
	$\nu(C{=}N)$ 1520 s	CD_3CN	5.55 s	3.65 q, 1.20 t	
3c	$\nu(NO_3^-)$ 1335 vs	$CDCl_3$	5.31 s	2.72 s	7.55 m
	$\nu(C{=}N)$ 1545 s				
3d	$\nu(BF_4^-)$ 1050 vs	$CDCl_3$	5.27 s	2.72 s	7.55 m
	$\nu(C{=}N)$ 1548 s				
4d	$\nu(C{\equiv}N)$ 2335 w,[c] 2305 w[c]	CD_3CN	5.55 s	3.18 s	1.95 s
	$\nu(BF_4^-)$ 1050 vs				
	$\nu(C{=}N)$ 1548 s				

[a] Spectra recorded in Nujol, hexachloro-1,3-butadiene, and potassium bromide. [b] Bands observed only in potassium bromide. [c] Bands observed only in mulls. [d] In ppm downfield of tetramethylsilane. [e] The methylene protons show as two quartets with an apparent difference of 2-4 Hz in chemical shift. An ABX_3 system should show four quartets. In this case, however, the outer peaks are expected to be very small. In only one case **2a** were these peaks observable.

upfield, and the frequency of the infrared C=N stretch is 20 cm^{-1} higher, compared to the ligand in **1a**. The electron-donating ability of the phosphine ligand of **3a** is greater than that of the iodide ligand of **1a**. As a result, the electron density in the carbamate ligand is greater in **3a** and this accounts for the ^1H NMR and infrared data.

The nitro complexes **1b** and **2b** are obtained by the reactions of the iodo complexes with sodium nitrite. The two infrared bands for the nitrite ligands at 1380–1370 and 1315–1312 cm^{-1} are consistent with the general trend observed in typical *N*-nitro complexes (MNO_2).[15] The asymmetric and symmetric stretching modes give rise to bands of approximately equal intensity at higher frequency than those observed for ionic nitrite ($\nu_{asym}NO_2^-$) = 1335 cm^{-1}, $\nu_{sym}(NO_2^-)$ = 1270 cm^{-1}).[16] *O*-Nitrito complexes (M—ONO), on the other hand, show one band (ν(N=O) at 1480–1450 cm^{-1} and a second band (ν(O—N)) at 1080–1050 cm^{-1}.[15]

The iodo complexes react with weaker nucleophiles in the presence of silver ion (Ag^+). Iodide is displaced from **1a** by acetonitrile in the presence of silver tetrafluoroborate. The infrared spectrum of the product **4d** suggests that the nitrile ligand is extremely labile. In mull spectra (Nujol and hexachloro-1,3-butadiene) bands consistent with N-coordinated acetonitrile[17] are observed. The mulls are the same color as the nitrile complex. The mixture with potassium bromide, however, is green, and no nitrile bands are observed in the spectrum of a pellet made from the mixture. A displacement reaction to give $CpCo(S_2CN(CH_3)_2)Br$ (which, by analogy to **1a**, should be green) and free acetonitrile is consistent with the observations. The ^1H NMR spectrum of **4d** includes the expected methyl singlets for the nitrile and carbamate ligands. The resonance for the cyclopentadienyl ligand, however, is shifted ~0.35 ppm downfield of that for the ligand **1a**.

Reactions of **1a** and **2a** with silver nitrate give the nitrato complexes, **1c** and **2c**. In mulls, the four infrared bands for nitrate are observed at frequencies close to the ranges reported for typical *O*-nitrato complexes:[18] 1530–1480, 1290–1250, 1030–970, and 805–780 cm^{-1}. In potassium bromide a fifth band, consistent with ionic nitrate ($\nu(NO_3^-)$ = 1380 cm^{-1}),[16] is present. The mulls are the same color as the nitrato complexes, but the potassium bromide mixtures are, once again, green. Anion exchange between metal nitrates and potassium bromide is known[19] and is proposed to account for the observations.

In the ^1H NMR the methyl singlet and ethyl ABX_3 pattern for the carbamate ligands of **1c** and **2c** are at chemical shifts similar to those for the ligands in the iodo complexes. The cyclopentadienyl singlets are shifted downfield. The downfield shifts of ~0.20 ppm in chloroform-d_1 reflect the increased ionic character of the Co–X bond and thus the greater formal positive charge on metal in **1c** and **2c**. The downfield shifts are even larger in acetonitrile-d_3, and the chemicals shifts are almost exactly the same as that observed for the ligand in **4d**. This similarity suggests that the nitrato complexes exist in acetonitrile as $[CpCo(S_2CNR_2)(CH_3CN)]NO_3$.

The labilities of the nitrate and nitrile ligands of **1c** and **4d** are confirmed by reactions with a variety of nuclephiles. Both complexes react with iodide or nitrite to give **1a** or **1b** upon mixing. Reactions with triphenylphosphine give **3c** and **3d**, respectively. Complex **3c** was characterized on the basis of spectroscopic data, most notably the strong band for ionic nitrate in the infrared in all media and the upfield shifted carbamate methyl singlet. Benzyl alcohol

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(15) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55.

(16) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1963.

(17) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

(18) Gatehouse, B. M.; Livingstone, S. E.; Nyholm, R. S. *J. Inorg. Nucl. Chem.* **1958**, *8*, 75.

(19) Meloche, V. W.; Kalbus, G. E. *J. Inorg. Nucl. Chem.* **1958**, *6*, 104.

also displaces acetonitrile from **4d**. There is no free acetonitrile present in a solution of **4d** in 1,2-dichloroethane by gas chromatography. A peak for acetonitrile is observed when a large excess of benzyl alcohol is added to the solution.

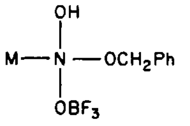
$$\mathbf{4d} + PhCH_2OH \rightarrow [CpCo(S_2CN(CH_3)_2)(HOCH_2Ph)]BF_4 + CH_3CN$$

Evidence for the displacement of nitrite from **1b** was also obtained. Reaction with iodide or triphenylphosphine gives **1a** or $[CpCo(S_2CN(CH_3)_2)(Ph_3P)]NO_2$ (**3b**). By chromatographic analysis (TLC, dichloromethane/methanol, 19:1), the reactions are fast and product/starting material mixtures are observed within 1 min of the beginning of the reactions. The product/starting material mixtures are still observed after longer reaction times and/or under more vigorous conditions, indicating that the reactions do not go to completion.

Displacement of nitrite by triphenylphosphine was unexpected in light of the reactions of $LCo(py)NO_2$ and triphenylphosphine.[20] In the presence of a large excess of pyridine, oxygen atom transfer occurs to give LCoNO and triphenylphosphine oxide. Although substitution does occur in the absence of excess pyridine, only $LCo(Ph_3P)NO_2$ is obtained and no evidence for further displacement is reported. For the reaction of **1b** with triphenylphosphine (1.0–1.5 equiv of Ph_3P, dichloromethane at room temperature or 1,2-dichloroethane at 60 °C, argon atmosphere) neither spectroscopic nor chromatographic evidence for triphenylphosphine oxide was observed.

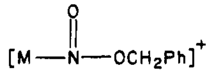
Complex **3b** could not be isolated as a pure compound, but spectroscopic evidence supports its formation. The infrared spectrum of the crude product from the reaction of **1b** with 1 equiv of triphenylphosphine in dichloromethane shows a band consistent with the nitrite counter ion of **3b** as well as the bands for the nitro ligand of **1b**. The ^1H NMR of a solution of **1b** (~70 mM) and triphenylphosphine (~35 mM) in chloroform-d_1 includes the multiplet for the phosphine aromatic protons, singlets for the cyclopentadienyl, and carbamate methyl protons of **1b** and a singlet at 2.71 ppm. By analogy to the spectra of the other phosphine complexes, the latter singlet is due to the carbamate protons of **3b**.

Oxidation of Benzyl Alcohol. The oxidation of benzyl alcohol by mixtures of **1b** and boron trifluoride etherate ($BF_3\cdot Et_2O$) was expected to occur by nucleophilic attack of alcohol oxygen on coordinated nitrogen. Reaction at BF_3-activated nitro ligand to give the tetrahedral intermediate A was proposed for the oxidation of benzyl alcohol by $LCo(py)NO_2$ and $BF_3\cdot Et_2O$.[3] The metal-bound nitrous acid ester B could arise either by loss of "$HOBF_3^-$" from A or by the net abstraction of oxide from nitro ligand by BF_3 followed by reaction with benzyl alcohol. The latter pathway is suggested by the reactions of certain ruthenium complexes. $(bpy)_2RuClNO_2$ reacts with Lewis acids ($SnCl_4$, BF_3, $BF_3\cdot Et_2O$) to give $[(bpy)_2RuClNO]^{2+}$,[21] which in turn reacts with alkoxide in alcohol/acetonitrile to give $[(bpy)_2RuCl(N(O)OR)]^+$ (R = ethyl, isopropyl).[22]



$$M-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OBF_3}{|}}{N}}-OCH_2Ph$$

A



$$[M-\overset{\overset{\displaystyle O}{\|}}{N}-OCH_2Ph]^+$$

B

Table II. Stoichiometric Oxidation of Benzyl Alcohol[a]

oxidant	solvent[b]	PhCHO,[c] %
1b	$PhNO_2$	120
$PPNNO_2$	$PhNO_2$	140
$PPNNO_2$	DCE	120
1c	$PhNO_2$	170
$PPNNO_3$	$PhNO_2$	230[d]
$PPNNO_3$	DCE	215[d]

[a] Reactions at 60-65 °C under argon atmosphere; [oxidant] = 50 mM; mol ratio of oxidant/benzyl alcohol/$BF_3\cdot Et_2O$ = 1:25:5. [b] $PhNO_2$ = nitrobenzene; DCE = 1,2-dichloroethane. [c] Gas chromatographic yield after 10 and 45 min; % PhCHO = 100(mol of PhCHO/mol of oxidant). [d] Yield after 45 min.

Such mechanisms for **1b** are ruled out by a comparison of the results for oxidation by **1b** and $PPNNO_2$. Both reactions are fast and they proceed at similar rates. The yields of benzaldehyde are 120–140% after 10 min and do not increase with longer reaction times (Table II). Both reactions give a mixture of nitric and nitrous oxide and solid tetrafluoroborate products. The evolution of the gases is clearly visible in the clear yellow $PPNNO_2$ reaction mixtures but cannot be seen in the dark purple solutions obtained with **1b**. The reaction with $PPNNO_2$ gives $PPNBF_4$ in high yield and purity. The product from the reaction of **1b** contains cyclopentadienyl and dimethyldithiocarbamato ligands and tetrafluoroborate by infrared analysis. In contrast to the six-coordinate complexes **3d** and **4d**, the product is only slightly soluble in noncoordinating solvents. If triphenylphosphine is added to a suspension in 1,2-dichloroethane, the solid dissolves and **3d** is obtained. On the basis of these observations, the product could be $[CpCo(S_2CN(CH_3)_2)BF_4]_n$.

These similarities suggest that the effect of metal ($[CpCo(S_2CN(CH_3)_2)]^+$) on the reaction is little if any different than the effect of PPN^+. In contrast, the reactions of $TPPCo(py)NO_2$ (TPP = tetraphenylporphyrin) with benzyl alcohol and $BF_3\cdot Et_2O$[3] are quite different. The reaction was briefly reinvestigated. It was confirmed that the oxidation is slower than those with **1b** and $PPNNO_2$, the yield of benzaldehyde is only 100% (based on nitro complex), and the cobalt product is the nitrosyl complex TPPCoNO. Careful analysis of the gases above the final reaction mixture failed to show any evidence for nitric or nitrous oxide.

The similarities between the reactions with **1b** and $PPNNO_2$ suggest that nitrite is displaced from **1b** before benzyl alcohol is oxidized. While no evidence for displacement in the oxidation mixtures was obtained, BF_3 could catalyze and/or facilitate that reaction in much the same way that silver ion affects the reactions of **1a** with weak nucleophiles. Interaction of BF_3 with nitro would stabilize the transition state for Co–N bond cleavage, and subsequent reaction of nitrite would drive the reaction to completion. The reaction of **4d** with benzyl alcohol to give free acetonitrile is evidence for the existence of the $[ML]^+$ complex (M = $CpCo(S_2CN(CH_3)_2$; L = benzyl alcohol).

$$\mathbf{1b} + BF_3 \rightleftharpoons M\text{-}NO_2\cdot BF_3 \rightleftharpoons [M^{\delta+}\cdots NO_2^{\delta-}\cdot BF_3]^{\ddagger} \rightarrow NO_2^-\cdot BF_3 + M^+ \xrightarrow{L} [ML]^+ \quad (1)$$

The mechanism of the subsequent reaction of nitrite and benzyl alcohol is not known, but the literature provides some basis for speculation. For example, the reactions of nitrite with Lewis acids to give nitrosonium (NO^+) products are well-known.[23] Specifically, alkali-metal nitrites

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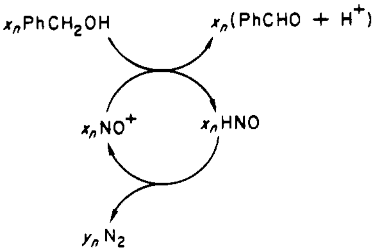
[20] Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 270.

[21] Godwin, J. P.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 2150.

[22] Walsh, J. L.; Bullock, R. M.; Meyer, T. *J. Inorg. Chem.* **1980**, *19*, 865.

Scheme I. Oxidation of Benzyl Alcohol via the NO^+/HNO Redox Couple[a]



[a] $x_n = (1/3)^n$; $y_n = (1/3)^{(n+1)}$; $n = 0 - \infty$ (for example, $n = 0$ for first cycle, $n = 1$ for second cycle, and so forth).[28]

($M'NO_2$) react with BF_3 to give nitrosonium tetrafluoborate (eq 2). While NO^+ reacts with simple alcohols to give

$$3M'NO_2 + 8BF_3 \rightarrow 3NOBF_4 + 3M'BF_4 + B_2O_3 \quad (2)$$

nitrous acid esters, alcohols that are activated to α-hydride abstraction are oxidized. Benzyl alcohol in particular is oxidized to benzaldehyde in 62% yield by $NOBF_4$ in dichloromethane (eq 3).[24] The nitrosyl hydride (HNO)

$$PhCH_2OH + NOBF_4 \xrightarrow{CH_2Cl_2} PhCHO + HNO + HBF_4 \quad (3)$$

product is not stable in the reaction mixture but reacts with NO^+ to give nitric oxide[25] or dimerizes to give hyponitrous acid ($H_2N_2O_2$) which decomposes to nitrous oxide (eq 4–6).[26]

$$HNO + NO^+ \rightarrow 2NO + H^+ \quad (4)$$

$$2HNO \rightleftharpoons H_2N_2O_2 \quad (5)$$

$$H_2N_2O_2 \rightarrow N_2O + H_2O \quad (6)$$

Reactions 1–6 account for the observed reaction products: benzaldehyde, $[CpCo(S_2CN(CH_3)_2)BF_4]_n$, and nitric and nitrous oxide. The yield of benzaldehyde predicted on the basis of those nitrogen oxide products, however, is only 50–100%. The oxidation is a two-electron process. The reduction of nitrite to nitric oxide requires one electron while reduction to nitrous oxide requires two electrons (eq 7 and 8). When these redox reactions are balanced, the predicted yields are given by the stoichiometries of the reactions.

$$PhCH_2OH + 2NO_2^- + 2H^+ \rightarrow PhCHO + 2NO + 2H_2O \quad (7)$$

$$PhCH_2OH + 2NO_2^- + 2H^+ \rightarrow 2PhCHO + N_2O + 3H_2O \quad (8)$$

The observed yields of benzaldehyde require further reduction. A three-electron process giving dinitrogen (unobservable by infrared) as the final product is consistent with the chemistry of hyponitrous acid. Decomposition to N_2 and nitrous and/or nitric acid is known to occur under certain conditions (eq 9 and 10).[27] The nitrite

$$3H_2N_2O_2 \rightarrow 2N_2 + 2HNO_2 + 2\,H_2O \quad (9)$$

$$H_2N_2O_2 + HNO_2 \rightarrow N_2 + HNO_3 + H_2O \quad (10)$$

Table III. Catalytic Oxidation of Benzyl Alcohol by Nitrate Oxidants[a]

oxidant	% PhCHO[b] 10 min	60 min	120 min
1c	210	320	355
$PPNNO_3$	100	335	400

[a] Reactions in nitrobenzene at 60–65 °C under 1 atm of oxygen; [oxidant] = 50 mM; mol ratio of oxidant/benzyl alcohol/$BF_3 \cdot Et_2O$ = 1:25:5. [b] Gas chromatographic yields; % PhCHO = 100(mol of PhCHO/mol of oxidant).

(or nitrate, vida infra) thus formed would be cycled back into the oxidation scheme via reaction 2, and the results can be rationalized by a cyclic mechanism based on the NO^+/HNO redox couple (Scheme I). One equivalent of oxidant is initially formed by reaction 1. During the oxidation, 0.33 equiv of oxidant and N_2 are formed in each cycle by decomposition of HNO and the predicted yield of benzaldehyde is thus 150% (based on nitrite).[28] To the extent that nitric and nitrous oxide are formed, the observed yield is expected to fall below that maximum value.

The reaction of **1c** with benzyl alcohol and $BF_3 \cdot Et_2O$ gives the same products as the reaction of **1b**. The yield of benzaldehyde is slightly higher (Table II). The reaction of $PPNNO_3$, however, shows an apparent induction period. Gas evolution is not observed until 20–30 min after $BF_3 \cdot Et_2O$ is added to the reaction mixture. After ~30 min benzaldehyde is produced in 40–50% yield. In the next 10–15 min, the reaction proceeds to give benzaldehyde in >200% yield, a mixture of nitric and nitrous oxide and $PPNBF_4$. Attempts to initiate the reaction with species known to initiate nitric acid oxidations[29] failed. Added nitrite or acid ($PPNNO_2$ or trifluoroacetic acid, ~5 mol %) affected neither the length of the induction period nor the amount of benzaldehyde produced during that time.

Nitrate is readily displaced from **1c** by weak nucleophiles in solution. Displacement in the oxidation mixture should be more facile than the displacement of nitrite from **1b** and the effect of BF_3 on those reactions should be the same. The reactions of nitrate with Lewis acids to give NO^+ products are also well-known.[30] Alkali-metal nitrates ($M'NO_3$) react with BF_3 to give $NOBF_4$ and oxygen (0.5 equiv) (eq 11).[23b]

$$3M'NO_3 + 8BF_3 \rightarrow 3NOBF_4 + {}^3/_2O_2 + 3M'BF_4 + B_2O_3 \quad (11)$$

A scheme based on the NO^+/HNO redox couple also accounts for these results. One equivalent of oxidant and 0.5 equiv of oxygen are initially formed by reaction 11. Regeneration of oxidant and formation of dinitrogen can occur by decomposition of HNO as before. Oxidant can also be regenerated by reactions involving oxygen. Nitric oxide reacts with oxygen to give nitrogen dioxide, which is known to react with BF_3 to give $NOBF_4$.[31] The reaction of nitrosyl hydride with oxygen to give nitrous acid[32] is a second possibility (eq 12–14). The amount of oxygen produced is dictated by reaction 11 and a net five-electron

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(23) (a) Beckham, L. J.; Fessler, W. A.; Kise, M. A. *Chem. Rev.* **1951**, *48*, 319. (b) Scott, R. N.; Shriver, D. F. *Inorg. Chem.* **1966**, *5*, 158 and references therein.

(24) Olah, G. A.; Ho, T.-L. *Synthesis* **1976**, 609.

(25) Strojny, E. J.; Iwamasa, R. T.; Frevel, L. K. *J. Am. Chem. Soc.* **1971**, *93*, 1171.

(26) Olah, G. A.; Salem, G.; Staral, J. S.; Ho, T.-L. *J. Org. Chem.* **1978**, *43*, 173.

(27) Buchholz, J. R.; Powell, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 2350.

(28) The amount of benzaldehyde formed is mol of PhCHO = $\sum_{n=0}^{\infty}(1/3)^n = 1.5$ and the amount of N_2 formed is mol of $N_2 = \sum_{n=1}^{\infty}(1/3)^n = 0.5$. The balanced reaction equation (neglecting hydrolysis products derived from oxide, protons, and BF_3) is $1.5\,PhCH_2OH + NO_2^- \rightarrow 1.5PhCHO + 0.5N_2$.

(29) Ogata, Y.; Sawaki, Y.; Matsunaga, F.; Tezuka, H. *Tetrahedron* **1966**, *22*, 2655.

(30) Kalbandkeri, R. G.; Padma, D. K.; Varsudeva Murthy, A. R. *Z. Anorg. Allg. Chem.* **1979**, *450*, 103.

(31) Ray, A. B. *Inorg. Chem.* **1967**, *6*, 110 and references therein.

(32) Ross, D. S.; Hum, G. P. *Gov. Rep. Announce. Index (U.S.)* **1980**, *80*, 335.

process occurs giving benzaldehyde in a predicted yield of 250% (based on nitrate).

$$NO + {}^1/_2O_2 \rightarrow NO_2 \qquad (12)$$

$$6NO_2 + 8BF_3 \rightarrow 6NOBF_4 + {}^3/_2O_2 + B_2O_3 \qquad (13)$$

$$HNO + {}^1/_2O_2 \rightarrow HNO_2 \qquad (14)$$

Consistent with this explanation, the oxidation by the nitrate oxidants is catalytic, with respect to oxidant, in the presence of oxygen. The two catalytic reactions have similar rate profiles (Table III). Reactions at rates comparable to those observed for the stoichiometric oxidations ($\sim$8 mol PhCHO/mol oxidant^{-1}/h^{-1}) are observed for the first 10–15 min. Thereafter, the rates decrease and the final yields of $\sim$400% are obtained after 2 h.

Tovrog et al. reported that TPPCo(py)NO_2 disproportionated in the presence of $BF_3{\cdot}Et_2O$ to give the corresponding nitrosyl and nitrate complexes and that this mixture oxidized benzyl alcohol to benzaldehyde.[3] We reinvestigated the reaction and, once again, found no evidence for nitric or nitrous oxide by infrared spectroscopy.

In summary, displacement of X from $CpCo(S_2CNR_2)X$ is facile and dominates the reactions of the nitro and nitrato complexes with oxidizable organic substrates. Cationic phosphine complexes are obtained from **1b** and **1c** by reaction with triphenylphosphine, and the substrate is not oxidized. The redox reactions involving benzyl alcohol do not involve metal-bound nitrogen oxide ester intermediates but can be rationalized by schemes (e.g., Scheme I) based on the NO^+/HNO redox couple. Our results indicate that criteria for establishing oxidation by that redox couple are observation of (1) nitric and nitrous oxide products, (2) metal tetrafluoborate products without nitrogen oxide ligands, and (3) more than 1 equiv of product/mol of oxidant.

Registry No. **1a**, 87101-28-8; **1b**, 87101-30-2; **1c**, 87101-32-4; **2a**, 87101-27-7; **2b**, 87101-31-3; **2c**, 87101-33-5; **3a**, 87101-29-9; **3c**, 87101-34-6; **3d**, 87101-35-7; **4d**, 87101-37-9; (PPN)NO_2, 65300-05-2; (PPN)NO_3, 38011-35-7; $PhCH_2OH$, 100-51-6; PhCHO, 100-52-7.

Cumulenes as Ligands.[1] (η^2-Butatriene)platinum(0) Complexes, a New Structural Class of Cumulene Complexes

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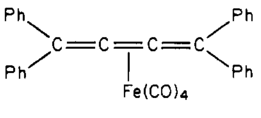
Displacement of ethylene from bis(triphenylphosphine)(ethylene)platinum(0) by four different butatrienes led to four new π complexes. In contrast to known butatriene complexes, the IR, ^{1}H NMR, and ^{31}P NMR spectra of these platinum compounds clearly show that the metal is bound to a terminal unsaturation of the triene. The π-bonding nature of the ligand attachment is indicated by the fast atom bombardment mass spectra and also ligand exchange reactions involving maleic anhydride. Attempts to produce binuclear platinum complexes were unsuccessful, but the platinum fragment may be replaced by rhodium upon reaction with Wilkinson's catalyst. These results are discussed in detail.

Olefin complexes comprise the oldest class of organometallic compounds, with the first reported olefin complex, Zeise's salt,[2] containing platinum. This metal has continued to be the most popular choice for producing π complexes.[3] Hartley has proposed a simple classification of olefin and acetylene π complexes,[4] with class S species modeled by the square-planar Zeise's salt and class T represented by the trigonal-planar compound bis(triphenylphosphine)(ethylene)platinum (**1**).

All of the known butatriene π complexes can be classified by using Hartley's scheme. For instance, the crystal structure of (tetraphenylbutatriene)tetracarbonyliron (**2**) reported by Bright and Mills[5] shows the trigonal-bipyramid coordination sphere of a typical pentacoordinate class T compound. West has reported the structure of a (diquinoethylene)rhodium complex (**3**)[6] that is in class S. We recently reported a crystal structure of a (butatriene)rhodium complex (**4**)[7] which also is a class S species.



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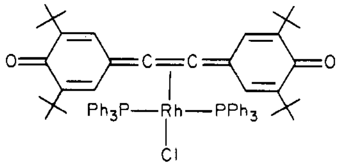

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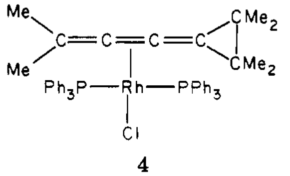

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[1] Third paper in a series. Part 2: White, M. R.; Stang, P. J. *Organometallics* **1983**, *2*, 0000. Abstracted in part from the Ph.D. dissertation of Mitchell R. White, The University of Utah, 1983.

[2] (a) Zeise, W. C. *Mag. Pharm.* **1830**, *35*, 105–108. (b) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science: London, 1973.

[3] Hartley, F. R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 39, pp 471–762.

[4] Hartley, F. R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 596–606.

[5] Bright, D.; Mills, O. S. *J. Chem. Soc. A* **1971**, 1979–1982.

[6] Hagelee, L.; West, R.; Calabrese, J.; Norman, J. *J. Am. Chem. Soc.* **1979**, *101*, 4888–4892.

[7] Stang, P. J.; White, M. R.; Maas, G. *Organometallics* **1983**, *2*, 720.