TABLE II

HALF-WAVE POTENTIAL OF THE Cr(II)–EDTA COMPLEX

[Cr(II)] = 6.02×10^{-4} *F*, [EDTA] = 3.90×10^{-2} *F*, [KCl] = *ca.* 0.1 *F*

pH	$-E_{1/2}$, v. *vs.* s.c.e.	pH	$-E_{1/2}$, v. *vs.* s.c.e.
4.140	1.244	6.717	1.234
4.360	1.226	7.025	1.235
5.062	1.227	7.370	1.240
5.340	1.227	8.042	1.270
5.504	1.227	9.041	1.318
5.716	1.226		
6.026	1.230	9.620	1.349
6.312	1.231	10.052	1.372

(II)–EDTA system and the spectrophotometeric data for the Cr(III)–EDTA system.[8] The electrode reactions proposed for the various pH ranges are

$$\text{pH} < 4;\ \text{Cr(HY)(H}_2\text{O)}^- = \text{CrY(H}_2\text{O)}^- + \text{H}^+ + \text{e}$$

$$\text{pH 4–6};\ \text{CrY(H}_2\text{O)}^{-2} = \text{CrY(H}_2\text{O)}^- + \text{e}$$

$$\text{pH 8–10};\ \text{CrY(H}_2\text{O)}^{-2} = \text{CrY(OH)}^{-2} + \text{H}^+ + \text{e}$$

$$\text{pH} > 11;\ \text{CrY(OH)}^{-3} = \text{CrY(OH)}^{-2} + \text{e}$$

From the half-wave potential in the pH range 4–6, where the total ionic strength was adjusted to 0.1 *F*, and the previously determined formation constant of the Cr(II)–EDTA complex, the formation constant of the Cr(III)–EDTA complex can be calculated in the usual way.[9] Unfortunately the half-wave potential of the Cr(II)/Cr(III) couple in noncomplexing media includes a substantial overvoltage. Therefore the value determined by Grube and Breitinger[10] was used, $E^0 = -0.412$ v. *vs.* n.h.e. at 19°. The value obtained, $\log K_f = 23.40$, is in line with earlier predictions.

Discussion

With this report, we can now list the formation and acidity constants of all divalent metal–EDTA complexes of the first transition series. In Table III, these values are compared with the sum of the first and second ionization potentials of the metals.

TABLE III

FORMATION AND ACIDITY CONSTANTS OF EDTA COMPLEXES OF FIRST TRANSITION SERIES

Temperature = 20°, μ = 0.1 *F*

Metal	$\log K_f$	pK^H	E_2[a]	$E_1 + E_2$[b]
V(II)	12.70	3.5	338	493
Cr(II)	13.61	3.00	380	536
Mn(II)	13.58	3.1	361	532
Fe(II)	14.33	2.8	373	554
Co(II)	16.31	3.0	393	574
Ni(II)	18.56	3.2	418	594
Cu(II)	18.79	3.0	468	646
Zn(II)	16.26	3.0	414	631

[a] Second ionization potential, kcal./mole. [b] First plus second ionization potentials, kcal./mole.

The stabilization of the Cr(II) complex by the ligand field effect makes the Cr(II) more stable than the Mn(II) complex, although this effect is not as extreme as for the Ni(II) and Cu(II) complexes when compared to the Zn(II) complex with its d^{10} configuration. As is the case with the other complexes of this group (except for V(II)) the pK^H is within the range 3.0 ± 0.2. Following Higginson's argument,[11] we propose a quinquedentate structure for the Cr(II)–EDTA complex, in a distorted octahedron with a water molecule occupying the less stable d_{z^2} position.

Acknowledgment.—The magnetic measurements reported herein were made by Mr. R. Garber.

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(8) C. Furlani, G. Morpurgo, and G. Satori, *Z. anorg. allgem. Chem.*, **303**, 1 (1960).

(9) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, New York, N. Y., 1952.

(10) G. Grube and A. Breitinger, *Z. Elektrochem. angew. physik. Chem.* **33**, 112 (1927).

(11) W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).

CONTRIBUTION FROM THE MELLON INSTITUTE
PITTSBURGH, PENNSYLVANIA

Metal Nitrosyls. I. Triphenylphosphine Nitrosyl Nickel Complexes[1]

BY ROBERT D. FELTHAM

Received March 21, 1963

The preparation and properties of some stable nitrosyl nickel complexes of the type NiXNOL_2 are reported. Several new methods for preparing these compounds are also discussed.

Methods for preparing nitrosyl nickel compounds have been known for quite a long time,[2–4] but the composition of the materials obtained from these reactions was uncertain. This uncertainty was due to the reactivity of the compounds formed in these reactions. With the exception of nitrosylcyclopentadienylnickel,[5] the first relatively stable compound, $\text{NiBrNO[(C}_6\text{H}_5)_3\text{P]}_2$, has only been briefly described.[6] Subse-

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(1) This research was sponsored by The International Nickel Company, Inc.

(2) R. L. Mond and A. E. Wallis, *J. Chem. Soc.*, **121**, 32 (1922).

(3) H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfrengle, *Liebigs Ann.*, **482**, 161 (1930).

(4) J. S. Anderson, *Z. anorg. allgem. Chem.*, **229**, 357 (1936).

(5) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(6) R. D. Feltham, *ibid.* **14**, 307 (1960).

quently a number of related compounds have also been reported.[7–9]

This paper describes in more detail the synthesis and reactions of compounds with the general formula $NiXNO[(C_6H_5)_3P]_2$ where X is Cl^-, Br^-, or I^-. The synthesis of these compounds in tetrahydrofuran (THF) can be qualitatively represented by the equation

$$NiX_2[(C_6H_5)_3P]_2 + aNaNO_2 + b(C_6H_5)_3P \xrightarrow{THF} NiXNO[(C_6H_5)_3P]_2 + c(C_6H_5)_3PO + dNaBr \quad (1)$$

although arguments presented later indicate that the mechanism of the process is quite different from that implied by the above equation.

In the presence of $(C_6H_5)_3P$ the compound $NiBrNO[(C_6H_5)_3P]_2$ reacts with a number of silver salts as indicated by the equation

$$NiBrNO[(C_6H_5)_3P]_2 + AgY + (C_6H_5)_3P \longrightarrow AgBr\cdot(C_6H_5)_3P + NiYNO[(C_6H_5)_3P]_2 \quad (2)$$

where Y may be OCN^-, $CH_3CO_2^-$, NO_3^-, NO_2^-, and $N_2O_2^{2-}$. The hyponitrite complex $\{NiNO[(C_6H_5)_3P]_2\}_2N_2O_2$ was found to be unstable. It decomposed during attempts at isolation and purification, giving in methanol the alcoholate $[NiOCH_3(NO)(C_6H_5)_3P]_2$.

It is important to note that the complex $NiBr_2[(n\text{-}C_4H_9)_3P]_2$, containing a tertiary aliphatic phosphine, reacts with $NaNO_2$ in alcohol in quite a different manner than does the tertiary aromatic phosphine complex in THF. The reaction is well represented by the equation

$$NiBr_2[(n\text{-}C_4H_9)_3P]_2 + 2NaNO_2 \xrightarrow{CH_3OH} Ni(NO_2)_2[(n\text{-}C_4H_9)_3P]_2 + 2NaBr \quad (3)$$

Experimental

The infrared spectra were obtained in Nujol and halocarbon mulls using a Beckman IR-4 spectrophotometer. The dipole moments were obtained using a WTW Dipolometer Model DW-01. The magnetic moments were measured by Dr. L. Vaska of this Institute using the Faraday method. The elemental analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colorado. The molecular weights were obtained in benzene using a Mechrolab vapor pressure osmometer.

Materials.—Triphenylphosphine obtained from the M and T Corp. was recrystallized from ethyl acetate. The sodium nitrite was Baker "Analyzed" reagent grade which had been dried under vacuum over Molecular Sieve No. 5A (Linde Company). All of the solvents except methanol were dried conveniently by use of $^1/_{16}$-in. pellets of No. 4A Molecular Sieve obtained from the Linde Company.

Since all of the compounds described herein are sensitive to oxygen and water, all operations were carried out under nitrogen. The nitrogen was the "H.P. Dry" grade obtained from the Linde Company.

1. **The Reactions of $NaNO_2$ with $NiX_2[(C_6H_5)_3P]_2$ (where X^- = Cl^-, Br^-, or I^-).**—The dihalobis(triphenylphosphine)nickel complex, prepared using the methods described by Venanzi,[10] was dissolved in peroxide-free tetrahydrofuran, sodium nitrite was added, and the mixture was refluxed. In the absence of excess triphenylphosphine the yields based on the nickel complex added were 50%. When one mole of triphenylphosphine per mole of Ni was added either before, during, or after reflux the yields were increased to 80%. The time of reflux was varied but periods longer than 30 to 40 min. had no effect on the yield. Although methanol, ethanol, dimethoxyethane, and chloroform were tried as reaction media, only THF and dimethylformamide led to the formation of the compound described below. The only compound other than $NiXNO[(C_6H_5)_3P]_2$ which was isolated from these reactions was $(C_6H_5)_3PO$.

In a typical experiment 6.73 mmoles of $NiBr_2[(C_6H_5)_3P]_2$ and 6.75 mmoles of $(C_6H_5)_3P$ were dissolved in 50 ml. of THF, 115 mmoles of dry, freshly ground $NaNO_2$ was added, and the solution was refluxed for 35 min. on a steam bath. After the solution was cooled, filtered, and evaporated to 35 ml., the addition of 25 ml. of *n*-hexane gave a blue oil. Separation of the oil and treatment with 50 ml. of cold methanol gave 5.69 mmoles (3.94 g.) of $NiBrNO[(C_6H_5)_3P]_2$. The yield based on the quantity of $NiBr_2[(C_6H_5)_3P]_2$ used was 85% in the above experiment. The compound was purified by recrystallization from benzene–hexane mixtures. Experiments involving other nickel halide complexes were carried out in an analogous manner.

$NiBrNO[(C_6H_5)_3P]_2$: m.p. 209–210° dec.; color, blue. *Anal.* Calcd.: C, 62.36; H, 4.37; N, 2.03; Ni, 8.48; O, 2.31; P, 8.94; mol. wt., 693.2. Found: C, 62.16; H, 4.26; N, 2.06; Ni, 8.48; O, 2.32; P, 8.4; mol. wt., 710 (in benzene).

$NiClNO[(C_6H_5)_3P]_2$: yield (above procedure), 44%; m.p. 200–203° dec.; color, blue. *Anal.* Calcd.: C, 66.65; H, 4.66; Cl, 5.46; N, 2.16; Ni, 9.05; O, 2.47; P, 9.55; mol. wt., 649. Found: C, 67.22; H, 4.71; Cl, 5.55; N, 2.16; Ni, 8.98; O, 2.58; P, 9.19; mol. wt., 626 (in benzene).

$NiINO[(C_6H_5)_3P]_2$: yield (above procedure), 77%; m.p. 190–193° dec.; color, blue. *Anal.* Calcd.: C, 58.40; H, 4.09; N, 1.90; Ni, 7.94; O, 2.16; P, 8.38; mol. wt., 740. Found: C, 58.74; H, 4.23; N, 1.82; Ni, 8.08; O, 2.36; P, 8.0; mol. wt., 730 (in benzene).

2. **The Reaction of $NiBrNO[(C_6H_5)_3P]_2$ with Silver Salts.**—In a typical experiment a mixture of 17 mmoles of $NiBrNO[(C_6H_5)_3P]_2$, 17 mmoles of $(C_6H_5)_3P$, and 20 mmoles of AgOCN in 100 ml. of methanol was stirred for 2 days at 25°. After the insoluble material was filtered off and dissolved in 100 ml. of benzene, the benzene-insoluble $AgBr(C_6H_5)_3P$ was then removed by filtration and 100 ml. of *n*-hexane was added to the filtrate to precipitate $Ni(OCN)(NO)[(C_6H_5)_3P]_2$. After two recrystallizations from 50% benzene–*n*-hexane, the yield of purified $Ni(OCN)(NO)[(C_6H_5)_3P]_2$ was 83% based on the $NiBrNO[(C_6H_5)_3P]_2$ used. The same method using silver acetate, nitrate, and nitrite was applied to give the compounds listed below.

$Ni(OCN)(NO)[(C_6H_5)_3P]_2$: color, blue. *Anal.* Calcd.: C, 67.81; H, 4.61; N, 4.29; Ni, 8.96; O, 4.88; P, 9.45; mol. wt., 655. Found: C, 68.18; H, 4.70; N, 4.36; Ni, 8.90; O, 5.00; P, 9.2; mol. wt., 648 (in benzene).

$Ni(NO_3)(NO)[(C_6H_5)_3P]_2$: color, blue. *Anal.* Calcd.: C, 64.02; H, 4.48; N, 4.15; Ni, 8.69; O, 9.50; P, 9.16; mol. wt., 675. Found: C, 64.11; H, 4.68; N, 3.85; Ni, 8.34; O, 9.05; P, 7.3; mol. wt., 675 (in benzene).

$Ni(NO_2)(NO)[(C_6H_5)_3P]_2$: color, blue. *Anal.* Calcd.: C, 65.58; H, 4.59; N, 4.25; Ni, 8.90; O, 7.28; P, 9.40; mol. wt., 659. Found: C, 65.33; H, 4.46; N, 4.40; Ni, 8.88; O, 7.52; P, 9.39; mol. wt., 673 (in benzene).

$Ni(CH_3CO_2)(NO)[(C_6H_5)_3P]_2$: color, blue. *Anal.* Calcd.: C, 67.89; H, 4.95; N, 2.08; Ni, 8.74; O, 7.13; P, 9.21; mol. wt., 672. Found: C, 67.24; H, 5.92; N, 1.69; Ni, 9.18; O, 7.08; P, 8.7.

Silver hyponitrite appeared to react in a manner analogous to that of the silver salts listed above, but the instability of the resulting complex prevented its isolation and characterization. For example, a mixture of 8.4 mmoles of $Ag_2N_2O_2$, 17.2 mmoles of $NiBrNO[(C_6H_5)_3P]_2$, and 16.0 mmoles of $(C_6H_5)_3P$ was stirred with 200 ml. of oxygen-free methanol for 2.5 hr. The blue solid was filtered off and dried. This material was dissolved in 100 ml. of benzene and filtered. The filtrate was evaporated to dryness and extracted once with 350 ml. of methanol. The material was redissolved in 50 ml. of benzene, filtered, and 50 ml.

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[7] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 2259 (1961).

[8] W. Hieber and I. Bauer, *Z. Naturforsch.*, **16b**, 556 (1961).

[9] G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

[10] L. Venanzi, *ibid.*, 719 (1958).

TABLE I

DIPOLE AND MAGNETIC MOMENTS OF SOME NICKEL NITROSYL COMPLEXES

	$NiI(NO)[(C_6H_5)_3P]_2$	$NiBr(NO)[(C_6H_5)_3P]_2$	$Ni(NO_2)(NO)[(C_6H_5)_3P]_2$
Dipole moment, Debye units	. . .	6.28	. . .
χ molar[a]	-325×10^{-6}	-242×10^{-6}	-232×10^{-6}

[a] Uncorrected.

of *n*-hexane was added to the filtrate to give some well-formed blue crystals. An infrared spectrum of this material showed the presence of three strong bands not due to triphenylphosphine at 1710, 1680, and 1080 cm.$^{-1}$. The relative strength of the two nitrosyl bands at 1710 and 1680 cm.$^{-1}$ varied considerably from preparation to preparation. The strong band at 1080 cm.$^{-1}$ was only present when there was a nitrosyl band at 1680 cm.$^{-1}$. This unstable complex slowly liberates N_2O with the subsequent formation of a methoxide, presumably $[NiOCH_3(NO)(C_6H_5)_3P]_2$. The unstable complex with frequencies of 1080 and 1680 cm.$^{-1}$ could not be separated from the methoxide by recrystallization, extraction, or chromatography because of this continual decomposition. The final material from this reaction was always a mixture of two nitrosyl complexes as identified by their infrared frequencies at 1710 and 1680 cm.$^{-1}$.

$[NiN_2O_2(C_6H_5)_3P]_2$: color, blue; decomposes at room temperature. *Anal.* Calcd.: C, 56.7; H, 3.97; N, 7.36; Ni, 15.42; O, 8.40; P, 8.14. Found: C, 59.7; H, 4.75; N, 3.66; Ni, 15.40; O, 8.38; P, 8.11.

3. The Reaction of $NiBr_2[(n\text{-}C_4H_9)_3P]_2$ with $NaNO_2$.—A solution of 5 g. (5 mmoles) of $NiBr_2[(n\text{-}C_4H_9)_3P]_2$ in methanol was warmed on a steam bath with 6 g. (870 mmoles) of $NaNO_2$. The reaction of the maroon starting material was quite rapid and soon gave a canary-yellow solution. The excess $NaNO_2$ was filtered off and the methanol was evaporated on a steam bath. After recrystallization of the product from *n*-hexane yellow crystals were obtained. The infrared spectrum exhibits three strong absorptions in the infrared region at 1397, 1322, and 819 cm.$^{-1}$. These frequencies are almost identical with those of the corresponding *trans*-dinitrobistri(*n*-butylphosphine)platinum compound.[11]

$Ni(NO_2)_2[(n\text{-}C_4H_9)_3P]_2$: color, yellow; m.p. 137–138.5°. *Anal.* Calcd.: C, 51.95; H, 9.78; N, 5.04; Ni, 10.54; P, 11.13. Found: C, 52.70; H, 10.27; N, 5.20; Ni, 10.34; P, 11.15.

Results and Discussion

These nitrosyl complexes are all dark blue to purple in color and diamagnetic (Table I). The X-ray powder patterns are very similar to those of the dihalobis(triphenylphosphine)nickel complexes, which are known to be tetrahedral, and bear little resemblance to those of the *cis* and *trans* planar platinum and palladium compounds, Pt or $PdBr_2[(C_6H_5)_3P]_2$. This evidence along with the high extinction coefficients ($\epsilon \sim 500$) and the high dipole moment of the bromo nitrosyl complex suggests that these complexes are tetrahedral.

Two of the more likely courses for the reaction of sodium nitrite with dibromobis(triphenylphosphine)nickel are described below. One possibility is

$$NaNO_2 + NiBr_2[(C_6H_5)_3P]_2 \longrightarrow NiBrNO_2[(C_6H_5)_3P]_2 + NaBr \quad (4)$$

$$NiNO_2Br[(C_6H_5)_3P]_2 + (C_6H_5)_3P \longrightarrow (C_6H_5)_3PO + NiBrNO[(C_6H_5)_3P]_2 \quad (5)$$

There is some experimental evidence against this. First, a large excess of triphenylphosphine does increase the yield, but one can achieve the same effect by adding the excess phosphine *after* the reaction with $NaNO_2$ is complete. Second, triphenylphosphine will not react with $Ni(NO_2)_2\cdot(n\text{-}C_4H_9)_3P_2$ to give a nitrosyl, although CO has been reported to do so.[9] Another possibility is

$$NiBr_2[(C_6H_5)_3P]_2 + 2NaNO_2 \longrightarrow Ni(NO_2)_2[(C_6H_5)_3P]_2 + 2NaBr \quad (6)$$

$$Ni(NO_2)_2[(C_6H_5)_3P]_2 \longrightarrow Ni(NO_3)(NO)[(C_6H_5)_3P]_2 \quad (7)$$

$$Ni(NO_3)(NO)[(C_6H_5)_3P]_2 + NaBr \longrightarrow NiBr(NO)[(C_6H_5)_3P]_2 + NaNO_3 \quad (8)$$

This seems to be the most reasonable route for several reasons. First, the dinitro compound is formed in the case of the tri-*n*-butylphosphine complex. Second, the formation of triphenylphosphine oxide would be a side reaction. This would indicate that the only effect of excess phosphine would be to replace the phosphine used up in this side reaction and thus account for the independence of yields on large excess of triphenylphosphine. The difference between the alkyl and aryl phosphine complexes may also be explained by the second set of reactions. The alkyl phosphine nickel halide complexes are all *trans*-planar, whereas the aryl phosphine nickel halide complexes are tetrahedral. The formation of the nitrosyl requires the transfer of an oxygen of one nitrito (nitro) group to the other. Sterically, this is relatively easy in the case of a tetrahedral complex and difficult in the case of a *trans*-planar one.

The reaction of $NiBrNO[(C_6H_5)_3P]_2$ with silver salts is quite general. It was found that excess triphenylphosphine is necessary because $AgBr\cdot(C_6H_5)_3P$ is always formed in these reactions. The bromotriphenylphosphine silver complex is very insoluble in methanol and most of the other solvents used. It was therefore very easy to separate the nickel complexes from the silver by recrystallization. The reaction with $Ag_2N_2O_2$ was the only one from which the corresponding nickel nitrosyl complex could not be isolated. This silver compound reacted slowly due to its insolubility. The hyponitritotriphenylphosphinenitrosylnickel is unstable

TABLE II

INFRARED FREQUENCIES OF SOME NICKEL NITROSYL COMPLEXES

Compound	Frequency, cm.$^{-1}$ NO	Frequency, cm.$^{-1}$ Other[a]
$NiI(NO)[(C_6H_5)_3P]_2$	1735	
$NiBr(NO)[(C_6H_5)_3P]_2$	1735	
$Ni(OCN)(NO)[(C_6H_5)_3P]_2$	1715	2000 (s),[c] 760 (w)
$Ni(NO_3)(NO)[(C_6H_5)_3P]_2$	1725	1460 (s), 1280 (s), 1050 (w), 815 (m)
$Ni(ONO)(NO)[(C_6H_5)_3P]_2$	1730	1380 (s), 1105 (ms), 825 (m)
$Ni_2N_2O_2(NO)_2[(C_6H_5)_3P]_2$	1680	1080 (ms)
$[NiOCH_3NO(C_6H_5)_3P]_2$	1710	
$Ni(NO)(C_5H_5)$[b]	1843	640
$[NiI(NO)]_x$	1855	566[8]
$[NiBr(NO)]_x$	1870	569[8]

[a] Exclusive of triphenylphosphine. [b] Observed in the vapor phase. [c] s, strong; m, medium; w, weak.

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[11] J. Chatt, *et al.*, *J. Chem. Soc.*, 4073 (1959).

and decomposes only a little more slowly than it is formed. The resultant material was a mixture of the oxide and hyponitrite from which the hyponitrite could not be separated. The hyponitrite was identified by its nitrosyl band at 1690 cm.$^{-1}$ and an absorption band at 1080 cm.$^{-1}$ due to the hyponitrite group.[12]

The important infrared frequencies are listed in Table II along with those of other nitrosyl nickel compounds. The nitrosyl frequency is strongly dependent upon the coordinated ligands. A similar effect has been studied with metal carbonyls.[13] However, since the nitrosyl frequency is quite as dependent upon the anion (1735–1680 cm.$^{-1}$) as it is upon the phosphine (1855–1735 cm.$^{-1}$) (see also ref. 9), it is difficult to invoke the usual explanation of the back donation (π-bonding) by the metal to account for these frequency shifts. An alternative explanation is that the bonding between the nitrosyl group and the nickel atom is strongly dependent upon the relative energies of the d-orbitals of the nickel, which in turn are strongly affected by the surrounding ligand field. This is a subject which requires extensive investigation of a much wider range of metal nitrosyl complexes.

Acknowledgment.—The author wishes to thank Dr. L. Vaska for the magnetic measurements.

[12] L. Kuhn and E. R. Lippincott, *J. Am. Chem. Soc.*, **78**, 1820 (1956).

[13] M. Bigorgne, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 199.

CONTRIBUTION FROM THE MELLON INSTITUTE,
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Metal Nitrosyls. II. The Reaction of Nitric Oxide with Dicarbonylbis(triphenylphosphine)nickel[1]

BY ROBERT D. FELTHAM

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The reactions of nitric oxide with $Ni[CO]_2[(C_6H_5)_3P]_2$ and $Ni(CO)_3(C_6H_5)_3P$ are shown to lead to a variety of nitrosyl nickel compounds of the type $NiX(NO)L_2$. L is triphenylphosphine or solvent ligand and X^- includes $^1/_2O^{2-}$, OH^-, $^1/_2N_2O_2^{2-}$ NO_2^-, and CH_3O^-. Molecular weights show them to be four-coordinate.

The reaction between nickel carbonyl and nitric oxide has been investigated by several authors.[2-4] From some of our own preliminary experiments, it was clear that this reaction leads to a mixture of unstable products. In order to stabilize these complexes, the reaction was carried out between nitric oxide and triphenylphosphine carbonyl nickel complexes.

Experimental

The infrared spectra were run as Nujol and halocarbon mulls on a Beckman IR-4 spectrophotometer. Molecular weights were determined under nitrogen using a Mechrolab Model 301A vapor pressure osmometer or ebullioscopically in benzene. Elemental analyses were performed by the Huffman Microanalytical Laboratories, Wheatridge, Colorado. All oxygen analyses reported here were determined directly using the Untersaucher method. Analyses for N_2, NO, CO, N_2O, and CO_2 using gas–solid chromatography[5] were carried out by the Physical Measurements Laboratory of this Institute.

Materials.—Triphenylphosphine was obtained from the M and T Corp. and recrystallized from ethyl acetate. Nickel carbonyl, as obtained from the International Nickel Company, was used without further purification.

The nitric oxide as obtained from Matheson contained 1.5% N_2O, 0.2% CO_2, 1% N_2, and traces of NO_2. In order to remove all of the NO_2 as well as some of the other impurities, the nitric oxide was passed slowly over $^1/_{16}$-in. pellets of Molecular Sieve No. 5A (Linde Company) at −78°. It was found that this treatment removed all impurities except N_2 and traces of N_2O. Simply passing NO over NaOH does not adequately remove NO_2. The nitrogen used as inert atmosphere was the "H.P. Dry" grade as obtained from the Linde Company.

Dicarbonylbis(triphenylphosphine)nickel, $Ni[CO]_2[(C_6H_5)_3P]_2$, was prepared as described by Rose.[6] The compound was recrystallized from ethyl acetate and dried under vacuum. The complex was a white crystalline solid, m.p. 210° dec. (reported[6] m.p. 210–215° dec.). The infrared spectrum consisted of two bands at 2000 and 1935 cm.$^{-1}$ in the carbonyl region.

Tricarbonyltriphenylphosphinenickel, $Ni(CO)_3(C_6H_5)_3P$, was prepared using the method described by Meriwether[7] and was found to have bands at 2080 and 1920 cm.$^{-1}$ in the infrared region.

$Ni(CO)_3(C_6H_5)_3P$: color, white. *Anal.* Calcd.: Ni, 14.45. Found: Ni, 14.46.

Reactions with NO.—All operations were carried out under nitrogen and all reagents were carefully dried. The nickel complex to be used was placed in a round bottom flask of appropriate size and the solvent was added. The flask was evacuated to the vapor pressure of the solvent at room temperature (25°), and nitric oxide was added without stirring the solution until the pressure in the flask was equal to atmospheric pressure. The supply of NO was then shut off and the solution was magnetically stirred. Using this technique, the mole ratio of NO to Ni could be carefully controlled.

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[1] Presented in part at the 7th International Conference on Coordination Chemistry, Stockholm, Sweden, June, 1962. This work was sponsored by The International Nickel Company, Inc.

[2] H. Reihlen, A. Gruhl, G. v. Hessling, and O. Pfrengle, *Ann.*, **482**, 161 (1930).

[3] J. C. W. Frazer and W. E. Trout, *J. Am. Chem. Soc.*, **58**, 2201 (1936).

[4] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1775 (1959).

[5] M. Lefort and X. Tarrago, *J. Chromatog.*, **2**, 218 (1959).

[6] J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).

[7] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).