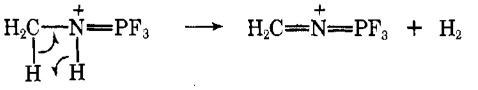
rine atom from the molecular ion can eliminate a molecule of hydrogen



$$\mathrm{H_2C{-}\overset{+}{N}{=}PF_3 \longrightarrow H_2C{=}\overset{+}{N}{=}PF_3 + H_2} \qquad (2)$$

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Nitrile Complexes of Zerovalent Nickel

By Chadwick A. Tolman

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Although nitrile complexes of a variety of metals in higher oxidation states have been well known for a long time,[1] nitrile complexes of metals in the zerovalent state are much more rare, the best known examples being $(CH_3CN)_nM(CO)_{6-n}$ where $n = 1, 2,$ or 3 and M = Cr, Mo, or W.[2] We wish to report the first examples of nitrile complexes of zerovalent nickel, of stoichiometry $(RCN)NiL_3$ where L is $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ and R is CH_3, CH_2CH_3, $n\text{-}C_4H_9$, or C_6H_5.

The preparation and properties of the three-coordinate nickel complex $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ (abbreviated NiL_3) have been previously reported.[3] Addition of an alkyl nitrile to a red-orange toluene solution of NiL_3 causes an immediate loss of color, attributed to the rapid reaction

$$\mathrm{RCN + NiL_3 \overset{K_1}{\rightleftharpoons} (RCN)NiL_3} \quad \text{fast} \qquad (1)$$

The stoichiometry of the adduct is shown by a ^{31}P nmr experiment in which valeronitrile was added to 0.06 mmol of NiL_3 in 0.3 ml of toluene. Addition of 0.03 mmol of RCN (RCN:Ni ratio 0.5:1) caused the sharp resonance of NiL_3 at −128.5 ppm (85% H_3PO_4)[4] to shift to −129.2 ppm. More RCN (RCN:Ni = 1:1) again gave a single sharp line, further shifted downfield to −130.7 ppm. Excess RCN (RCN:Ni = 2:1) had no further effect on the ^{31}P spectrum. Addition of free L to the same solution gave a second resonance at −130.0 ppm, the chemical shift of free ligand alone.[4] These observations show that (1) reaction 1 must be fast enough to average resonances of L in NiL_3 and in $(RCN)NiL_3$, (2) the reaction has an appreciable equilibrium constant, (3) species with more than one RCN are not involved, and (4) free ligand is not in rapid exchange with complexed.[5,6] With the addition of a large excess of L a new resonance at −129.3 ppm, assigned to NiL_4,[4] grew at the expense of the resonance due to $(RCN)NiL_3$, showing displacement of RCN according to reaction 2. Similar results were obtained with benzonitrile, except that C_6H_5CN was less easily displaced.

$$\mathrm{(RCN)NiL_3 + L \rightleftharpoons NiL_4 + RCN} \qquad (2)$$

Spectrophotometric experiments in which aceto-, propio-, or valeronitrile was added to a benzene solution of NiL_3 showed the disappearance of absorbance above 400 mμ and an isosbestic point at 356 mμ, as shown in Figure 1. Values of K_1 determined in a thermostated cell given as a function of temperature are: 10°, 510 ± 40; 25°, 230 ± 20; 40°, 120 ± 25. A plot of log K_1 against $1/T$ gives $\Delta H° = -9 \pm 1.5$ kcal/mol and $\Delta S° = -19 \pm 5$ eu.

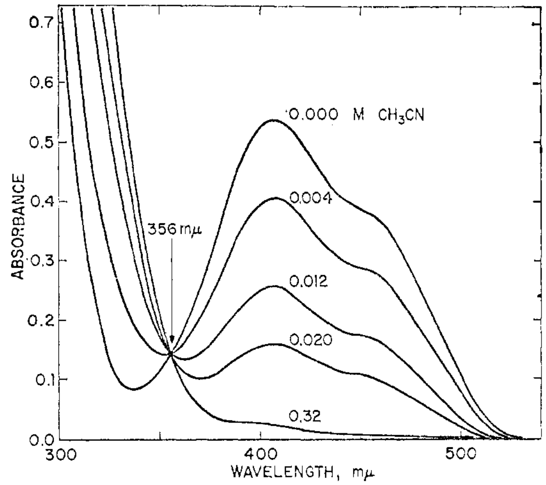

Figure 1.—Selected spectra for the addition of CH_3CN to 1.14×10^{-2} *M* $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ in benzene at ambient temperature; 0.1-mm cell.

The spectra with added benzonitrile were different, with an isosbestic point at 425 mμ; the final yellow-orange solution with excess C_6H_5CN showed an absorbance maximum at 396 mμ (ϵ 5.8 × 10^3 cm^{-1} M^{-1}). For benzonitrile $K_1 \approx 1000 \pm 400$ M^{-1}, in benzene at ambient temperature. The longer wavelength electronic band and the larger formation constant of benzonitrile compared to those of the alkyl nitriles are presumed to be consequences of electron delocalization which includes the benzene ring of the aromatic nitrile.

Infrared spectra of toluene solutions containing NiL_3 and excess CH_3CN showed a band at 2266 cm^{-1} due to ν_{CN} in $(CH_3CN)NiL_3$ in addition to a band of free CH_3CN at 2256 cm^{-1} ($\Delta\nu_{CN} = +10$ cm^{-1}). A similar solution with benzonitrile showed bands of $(C_6H_5CN)NiL_3$ and C_6H_5CN at 2217 and 2229 cm^{-1}, respectively ($\Delta\nu_{CN} = -12$ cm^{-1}). This is one of the few reported cases of a shift of ν_{CN} to lower frequency on complexation of benzonitrile.[7]

Analytically pure samples of $(RCN)NiL_3$ have not yet been prepared, owing to the ease with which they

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(1) R. A. Walton, *Quart. Rev., Chem. Soc.*, **19**, 126 (1965).

(2) G. R. Dobson, M. F. A. El Sayed, I. W. Stolz, and R. F. Sheline, *Inorg. Chem.*, **1**, 526 (1962).

(3) L. W. Gosser and C. A. Tolman, *ibid.*, **9**, 2350 (1970).

(4) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

(5) This behavior can be contrasted with that when C_2H_4 is added to a solution of NiL_3. In that case the reaction is $C_2H_4 + NiL_3 \rightleftharpoons (C_2H_4)NiL_2 +$ L and rapid exchange of free ligand with complexed occurs.[6]

(6) W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, **9**, 2354 (1970).

(7) R. E. Clark and R. C. Ford, *ibid.*, **9**, 227 (1970), recently reported $\Delta\nu_{CN} = -37$ and -15 cm^{-1}, respectively, for C_6H_5CN and CH_3CN in the complexes $(RCN)Ru(NH_3)_5{}^{2+}$.

dissociate. However, removal of excess CH_3CN under vacuum from a solution of NiL_3 in acetonitrile gave a brownish white solid foam, which dissolved in benzene to give an orange solution, in ether to give a yellow solution, and in hexane to give a light yellow solution.[8] In methanol the starting NiL_3 complex precipitated as a red powder. The proton nmr spectrum of the orange solution (C_6D_6) showed four resonances at τ 2.28, 3.16, 7.93, and 9.44 in a ratio of 9:27:27:3 as expected for the ortho H of L, unresolved meta and para H's of L, CH_3 of L, and CH_3CN, respectively, in the complex $(CH_3CN)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$. Addition of CH_3CN to the solution caused the highest field resonance to shift toward the free CH_3CN position at τ 9.29, without appreciably affecting the resonances due to L, in agreement with the very rapid exchange of free and complexed CH_3CN in eq 1 proposed on the basis of the ^{31}P experiments.

That nitrile complexes of Ni(0) form with other phosphorus ligands was shown by the rapid color change of a red toluene solution of $Ni(P(C_6H_5)_3)_3$ to yellow on addition of excess CH_3CN. We have been unable to see the ν_{CN} band of $(CH_3CN)Ni(P(C_6H_5)_3)_3$ in the infrared spectrum, possibly because it is masked by the free CH_3CN.

The formation of nitrile complexes of Ni(0) with the phosphorus ligands $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ or $P(C_6H_5)_3$ is facilitated since their three-coordinate nickel complexes have a free coordination position, ready to accept a nitrile to give the metal an 18-electron inert gas configuration. Four-coordinate nickel complexes, such as $Ni[P(OC_2H_5)_3]_4$, which do not dissociate detectably in solution,[4] show no evidence of complex formation with nitriles even when present in large excess.

Experimental Section

All preparations were done under an N_2 atmosphere in a vacuum Atmosphere drybox. The nickel complexes and their solutions are very sensitive to O_2 of air. The ^{31}P nmr spectra were recorded at 40.5 Mc using a Varian HA-100 spectrometer. Chemical shifts were measured using a concentric capillary of P_4O_6 and are reported with respect to 85% H_3PO_4, after subtracting 112.5 ppm from the measured values. Proton nmr spectra were recorded at 60 Mc on a Varian A-60 spectrometer using tetramethylsilane as an internal reference in C_6D_6. Infrared spectra were recorded with 0.1-mm NaCl cells using a Perkin-Elmer 221 spectrometer; spectra were calibrated with CO gas. Optical spectra were recorded with a Cary 14 spectrometer using quartz cells of 0.1- and 1-mm path length and a 1-mm thermostated cell (Optical Cell Co., Inc.). Water circulated from a Forma constant-temperature bath was used to maintain the temperature in the thermostated cell to ±0.5°.

The complexes $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$[3] and $Ni(P(C_6H_5)_3)_3$[9] were prepared by literature methods. The solvents and nitriles were reagent grade. The crude product $(CH_3CN)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ prepared by removal of excess CH_3CN under vacuum from $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ melted to a red liquid at 50–80° and blackened over 100° (sealed evacuated capillary). *Anal.* Calcd for $C_{65}H_{66}NNiO_9P_3$: C, 67.5; H, 5.8; N, 1.2; Ni, 5.1. Found: C, 66.0; H, 5.8; N, 1.2; Ni, 4.6.

Acknowledgments.—The author is indebted to Dr. W. C. Seidel for preparation of pure samples of the NiL_3 complexes and to Mrs. Jean L. Read for running the nmr spectra.

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[8] The dependence of the color of the solution on the solvent indicates that $(CH_3CN)NiL_3$ dissociates more extensively in more polar solvents. From the electronic spectra, we expect the pure $(CH_3CN)NiL_3$ complex to be colorless.

[9] B. Bogdanovic, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966).

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The Reaction of Metal Oxide Salts with Fluorinated Anhydrides[1]

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Recently, it was found[2] that chromium trioxide reacts with fluorinated anhydrides according to the equation

$$CrO_3 + (R_fCO)_2O = CrO_2(R_fCOO)_2 \qquad (1)$$

where $R_f = CF_3$, $ClCF_2$, or C_3F_7.

In our investigations with other chromium(VI) oxy compounds an attempt was made to replace the chloro group in $KCrO_3Cl$. Surprisingly it was found that, as well as replacing the chloro group, addition across the chromium–oxygen multiple bond occurred according to the equation

$$KCrO_3Cl + 2(CF_3CO)_2O \longrightarrow KCrO_2(CF_3COO)_3 + CF_3COCl \qquad (2)$$

We have studied other salt systems as well as other fluorinated anhydrides in order to determine the scope of this reaction. The results of this work are presented in Table I. It is seen that not only Cr(VI) salts but other group VIb oxy(transition metal) salts (with high positive oxidation states) are also reactive.

The new chromium salts in Table I are usually red-brown solids which are soluble in excess $(CF_3CO)_2O$ and are not extremely stable [*e.g.*, $K_2CrO_2(CF_3COO)_4$ decomposes above 150°] toward heat or light.

TABLE I

Salt	Anhydride	Product(s)
$KCrO_3Cl$	$2(CF_3CO)_2O$	$KCrO_2(CF_3COO)_3$ + CF_3COCl
$K_2Cr_2O_7$	$3(CF_3CO)_2O$	$2KCrO_2(CF_3COO)_3$
$K_2Cr_2O_7$	$3(ClCF_2CO)_2O$	$2KCrO_2(ClCF_2COO)_3$
K_2CrO_4	$2(CF_3CO)_2O$	$K_2CrO_2(CF_3COO)_4$
K_2CrO_4	$2(C_3F_7CO)_2O$	$K_2CrO_2(C_3F_7COO)_4$
Cs_2CrO_4	$2(CF_3CO)_2O$	$Cs_2CrO_2(CF_3COO)_4$
$(NH_4)_3Cr_2O_7$	$3(CF_3CO)_2O$	$2NH_4CrO_2(CF_3COO)_3$
Ag_2CrO_4	$2(CF_3CO)_2O$	$Ag_2CrO_2(CF_3COO)_4$
$PbCrO_4$	$2(CF_3CO)_2O$	$PbCrO_2(CF_3COO)_4$
Na_2MoO_4	$2(CF_3CO)_2O$	$Na_2MoO_2(CF_3COO)_4$
Na_2WO_4	$2(CF_3CO)_2O$	$Na_2WO_2(CF_3COO)_4$

All of the compounds are very water sensitive with the chromium compounds hydrolyzing according to the generalized equation

$$M_{1\,or\,2}CrO_2(R_fCOO)_{3\,or\,4} + 2H_2O = (1\text{ or }2)M^+ + CrO_4^{2-} + (3\text{ or }4)R_fCOO^- + 4H^+ \qquad (3)$$

($M^+ = K^+, Cs^+, NH_4^+$; $R_f = CF_3, ClCF_2, C_3F_7$). The infrared spectra were measured neat between NaCl windows and are listed in Table II. On the basis of the results of Sharp and coworkers[3] for anhydrous transition metal trifluoroacetates, the various absorption bands were assigned for the oxy(transition metal) trifluoroacetates. The COO asymmetric stretch occurs at 1670–1700 cm^{-1}, COO symmetric stretch at 1320–

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[1] Presented at the 25th Regional Meeting of the American Chemical Society, Seattle, Wash., 1970.

[2] J. N. Gerlach and G. L. Gard, *Inorg. Chem.*, **9**, 1565 (1970).

[3] M. J. Bailie, D. H. Brown, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc. A*, 3110 (1968).