a rate law is appropriate for a system in which either the oxidant or the reductant is partitioned into an inactive acidic form (having an acidity constant $K$) and an active basic form, with the two forms existing in comparable concentrations in 1 $M$ $H^+$. However, both $Ti(H_2O)_6^{3+}$ and the phenolic oxidants are very nearly completely protonated at this acidity. Moreover the observed twofold variation in $k_{obsd}$ when $(H^+)$ is increased from 0.02 to 1.0 $M$ appears to be far too great to be attributed to a medium effect. In short, the kinetic behavior of these hydroxy-substituted complexes conforms to no simple mechanistic picture.

(31) Such rate enhancements have been noted also for reactions of Eu(II)[10] and V(II)[9] but are less usual with these reductants.

(32) (a) A. Zanella and H. Taube, *J. Amer. Chem. Soc.*, **94**, 6403 (1972); (b) E. S. Gould, *ibid.*, **96**, 2373 (1974).

(33) For a summary of reduction potentials of carbonyl systems, see W. M. Clark, "Oxidation-Reduction Potentials of Organic Systems," Williams and Wilkins, Baltimore, Md., 1960, pp 497–505. No potentials for aldehydobenzoic acids appear to have been reported, but as aldehydes, they may be assumed to have values slightly greater than 0.2 V at 25°.

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# Synthesis of Some Rhodium(I) Complexes Containing Isocyanides and Phosphites, Phosphonites, or Phosphinites and Their Reactions with Cyanoolefins

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The synthesis of $[Rh(RNC)_2L_n]ClO_4$ (R = $p$-$CH_3OC_6H_4$ or $p$-$CH_3C_6H_4$; $n$ = 2, L = $P(OPh)_3$; $n$ = 3, L = $PPh(OMe)_2$ or $PPh_2(OMe)$), $[Rh(RNC)_2L_2(\text{cyanoolefin})]ClO_4$ (R = $p$-$CH_3OC_6H_4$ or $p$-$CH_3C_6H_4$; L = $P(OPh)_3$, $PPh(OMe)_2$, or $PPh_2(OMe)$; cyanoolefin = tetracyanoethylene (TCNE) or fumaronitrile (FN)), and $Rh(RNC)_2(P(OPh)_3)(\text{cyanoolefin})I$ (R = $p$-$CH_3OC_6H_4$ or $p$-$CH_3C_6H_4$; cyanoolefin = TCNE or FN) is described. Their ir and pmr spectra have been obtained to suggest their configurational behavior in solution. In the TCNE complexes TCNE may be coordinated rigidly to the rhodium atom perhaps in a trigonal-bipyramidal environment with axial isocyanides and equatorial phosphorus ligands. The five-coordinated complexes $[Rh(RNC)_2L_3]ClO_4$ (**2** and **3**; R = $p$-$CH_3OC_6H_4$ and $p$-$CH_3C_6H_4$; L = $PPh(OMe)_2$ and $PPh_2(OMe)$), undergo the dissociative exchange of L at higher temperatures. Temperature-dependent virtual coupling signals of $P$-OMe protons of $[Rh(RNC)_2(PPh(OMe)_2)_2(FN)]ClO_4$ (**9**) at lower temperatures are consistent with a gradual change of the interaction between FN and the rhodium atom with lowering temperature. Temperature-dependent pmr signals of FN protons of $Rh(RNC)_2(P(OPh)_3)(FN)I$ (**10**) at lower temperatures are interpreted in terms of a restricted rotation of FN in a time-averaged square pyramid. At higher temperatures **9** and **10** undergo the dissociative exchange of FN.

## Introduction

Cyanoolefins have widely been known to form rigid adducts with low-valent transition metal complexes containing tertiary phosphines and/or carbon monoxide.[1] Recently we have reported for the first time a series of nonrigid cyanoolefin adducts with some rhodium(I) isocyanide complexes.[2] This novel result will be related to the fact that isocyanides are known to be moderate $\sigma$ donors and are probably intermediate in $\pi$-acceptor capacity between phosphines and carbon monoxide.[3] Thus, it will be of interest to study the reactions of cyanoolefins with some rhodium(I) complexes containing ligands which may resemble isocyanides in coordinating ability.[4]

Here we report the preparation of some rhodium(I) complexes involving isocyanides and phosphites, phosphonites, or phosphinites and their reactions with tetracyanoethylene (TCNE) and fumaronitrile (FN).

## Experimental Section

Isocyanides[5] and phosphorus ligands[6] were prepared by literature methods. $[Rh(1,5\text{-}C_8H_{12})(P(OPh)_3)_2]ClO_4$ was also prepared according to the literature method.[7] $[Rh(1,5\text{-}C_8H_{12})L_3]ClO_4$ (L = $PPh(OMe)_2$ and $PPh_2(OMe)$) were synthesized in manners similar to that of the $P(OPh)_3$ complex. Preparations of the complexes were usually carried out under nitrogen at ambient temperature. Recrystallizations were done in air usually once but repeatedly in some cases (**1a**, **1b**, **3a**, **4a**, and **6b**) until satisfactory analytical data were obtained.

Many of the complexes were prepared by the similar procedures, so only a few representative examples are described in detail. Physical measurements were performed as described elsewhere.[2] The recrystallization solvents and analytical and physical data for the complexes are collected in Table I. Ir and pmr data are summarized in Table II.

**Preparation of the Starting Complexes. Bis(*p*-methoxyphenyl isocyanide)bis(triphenyl phosphite)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ (1a).** To a solution of $[Rh(1,5\text{-}C_8H_{12})(P(OPh)_3)_2]ClO_4$ (1430 mg, 1.5 mmol) in $CH_2Cl_2$ (20 ml) was added dropwise a solution of $p$-$CH_3OC_6H_4NC$ (410 mg, 3.0 mmol) in $CH_2Cl_2$ (5 ml). The color of the solution turned from orange to yellow. After being stirred for 1.5 hr, the solution was concentrated under reduced pressure. Addition of $C_2H_5OH$ afforded a yellow precipitate, which was filtered and recrystallized from $CH_2Cl_2$–$C_2H_5OH$ to give yellow plates of **1a** (1520 mg, 91%).

**Bis(*p*-methoxyphenyl isocyanide)tris(dimethyl phenylphosphonite)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_3]ClO_4$ (2a).** The product obtained from a reaction of $[Rh(1,5\text{-}C_8H_{12})(PPh(OMe)_2)_3]ClO_4$ (250 mg, 0.31 mmol) with $p$-$CH_3OC_6H_4NC$ (82 mg, 0.62 mmol) was recrystallized from $CH_2Cl_2$–ligroin (bp 70–90°) to afford yellow needles of **2a** (230 mg, 76%).

**Preparation of the TCNE Complexes. Bis(*p*-methoxyphenyl isocyanide)bis(triphenyl phosphite)(tetracyanoethylene)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$ (4a).** TCNE (26 mg, 0.2 mmol) was added to a solution of **1a** (224 mg, 0.2 mmol) in $CH_2Cl_2$ (5 ml). The solution was stirred for 1 hr, during which time the color of the solution changed from yellow to almost colorless. The product obtained upon concentration under reduced pressure was recrystallized from $CH_2Cl_2$–petroleum ether (bp 40–70°) to afford pale yellow crystals of **4a** (180 mg, 72%).

**Bis(*p*-methoxyphenyl isocyanide)bis(dimethyl phenylphosphonite)(tetracyanoethylene)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_2(TCNE)]ClO_4$ (5a).** A reaction of **2a** (94 mg, 0.12 mmol) with TCNE (15 mg, 0.12 mmol) gave a product, which was recrystallized from $CH_2Cl_2$–$C_2H_5OH$ to afford pale brown crystals of **5a** (45 mg, 50%).

**Iodobis(*p*-methoxyphenyl isocyanide)(triphenyl phosphite)(tetracyanoethylene)rhodium, $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(TCNE)I$ (7a).** To a solution of **1a** (76 mg, 0.7 mmol) in $CH_2Cl_2$ (2 ml) was added TCNE (9 mg, 0.7 mmol) and then NaI (13 mg, 0.9 mmol) in $C_2H_5OH$ (2 ml) and the mixture was stirred for 1 hr. The color of the solution changed from yellow to pale yellow and then to orange. Concentration under reduced pressure precipitated a product, which

Table I. Recrystallization Solvents and Analytical and Physical Data for the Complexes

| No. | Complexes[a] | Re-crystn sol-vents[b] | % carbon | | % hydrogen | | % nitrogen | | $\Lambda$[c] or mol wt[d] |
|---|---|---|---|---|---|---|---|---|---|
| | | | Calcd | Found | Calcd | Found | Calcd | Found | |
| 1a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ | A | 57.34 | 57.10 | 4.07 | 3.86 | 2.57 | 2.76 | 151 |
| 1b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ | A | 59.08 | 58.80 | 4.20 | 4.28 | 2.65 | 2.83 | 154 |
| 2a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_3]ClO_4$ | B | 48.43 | 48.87 | 4.91 | 4.71 | 2.90 | 3.07 | 177 |
| 2b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_3]ClO_4$ | B | 50.09 | 50.06 | 5.08 | 4.89 | 3.00 | 3.01 | 146 |
| 3a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_2(OMe))_3]ClO_4$ | A | 59.12 | 59.15 | 4.78 | 4.89 | 2.52 | 2.62 | 144 |
| 3b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh_2(OMe))_3]ClO_4$ | A | 60.86 | 61.18 | 4.93 | 5.29 | 2.58 | 2.65 | 146 |
| 4a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$ | C | 57.23 | 56.93 | 3.64 | 3.28 | 6.90 | 7.22 | 137 |
| 4b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$ | C | 58.77 | 58.00 | 3.74 | 4.06 | 7.09 | 7.02 | 106 |
| 5a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_2(TCNE)]ClO_4$ | A | 48.70 | 48.19 | 3.88 | 3.96 | 8.97 | 8.84 | 151 |
| 5b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_2(TCNE)]ClO_4$ | A | 50.42 | 50.09 | 4.02 | 4.09 | 9.29 | 9.06 | 203 |
| 6a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_2(OMe))_2(TCNE)]ClO_4$ | A | 56.01 | 55.72 | 3.93 | 3.98 | 8.17 | 8.12 | 140 |
| 6b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh_2(OMe))_2(TCNE)]ClO_4$ | A | 57.81 | 57.84 | 4.05 | 3.93 | 8.43 | 8.28 | 141 |
| 7a | $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(TCNE)I$ | C | 51.41 | 51.47 | 3.13 | 3.23 | 8.99 | 9.16 | 1007 (935) |
| 7b | $Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)(TCNE)I$ | C | 53.23 | 53.38 | 3.24 | 3.24 | 9.31 | 9.31 | 926 (903) |
| 8 | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(FN)]ClO_4$ | C | 57.62 | 57.30 | 3.97 | 4.09 | 4.80 | 4.55 | 128 |
| 9a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_2(FN)]ClO_4$ | D | 48.74 | 48.52 | 4.33 | 4.39 | 6.32 | 6.34 | 147 |
| 9b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_2(FN)]ClO_4\cdot FN$ | D | 51.48 | 51.41 | 4.33 | 4.24 | 9.00 | 8.94 | 144 |
| 10a | $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(FN)I$ | C | 51.60 | 51.51 | 3.53 | 3.41 | 6.33 | 6.50 | 711 (884) |
| 10b | $Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)(FN)I$ | C | 53.54 | 53.61 | 3.66 | 3.65 | 6.57 | 6.78 | 705 (852) |

[a] Abbreviations for ligands: $P(OPh)_3$ = triphenyl phosphite, $PPh(OMe)_2$ = dimethyl phenylphosphonite, $PPh_2(OMe)$ = methyl diphenylphosphinite, TCNE = tetracyanoethylene, and FN = fumaronitrile. [b] A = $CH_2Cl_2$–$C_2H_5OH$, B = $CH_2Cl_2$–ligroin (bp 70–90°), C = $CH_2Cl_2$–petroleum ether (bp 40–70°), and D = $CH_2Cl_2$–petroleum ether–ether. [c] Molar conductivity in $ohm^{-1}\ cm^2\ mol^{-1}$. [d] Measured in benzene at 37° by a Mechrolab vapor pressure osmometer. Calculated values in parentheses.

Table II. Ir and Pmr Data of the Complexes

| No. | Complexes | Ir,[a] $cm^{-1}$ | | Pmr, $\delta$,[e] ppm | | |
|---|---|---|---|---|---|---|
| | | $\nu$(NC)[b] | $\nu$(CN)[c] | $C_6H_4$[f] | $CH_3$ | *P*-OMe[g] |
| 1a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ | 2155s | | 6.77 6.71 | 3.78 | |
| 1b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ | 2155s | | *h* 6.70 | 2.36 | |
| 2a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_3]ClO_4$ | 2137 s, 2171 sh | | 6.68 6.44 | 3.73 | 3.50 s, br |
| 2b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_3]ClO_4$ | 2134 s, 2171 sh | | 7.00 6.41 | 2.29 | 3.50 s, br |
| 3a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_2(OMe))_3]ClO_4$ | 2128 s, 2160 sh | | 6.57 5.89 | 3.71 | 3.48 s, br |
| 3b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh_2(OMe))_3]ClO_4$ | 2131 s | | 6.91 5.96 | 2.26 | 3.48 s, br |
| 4a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$ | 2213 s, 2153 w | *d* | *h* 6.84 | 3.80 | |
| 4b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$ | 2219 s | *d* | *h* *h* | 2.41 | |
| 5a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_2(TCNE)]ClO_4$ | 2209 s | 2221 sh | 7.16 6.87 | 3.80 | 3.98 d |
| 5b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_2(TCNE)]ClO_4$ | 2207 s | 2221 sh | 7.27 7.21 | 2.38 | 3.98 d |
| 6a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_2(OMe))_2(TCNE)]ClO_4$ | 2205 s | 2223 m | 7.04 6.86 | 3.81 | 3.68 d |
| 6b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh_2(OMe))_2(TCNE)]ClO_4$ | 2202 s | 2221 sh | 7.22 6.99 | 2.69 | 3.68 d |
| 7a | $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(TCNE)I$ | 2204 s | 2228 m | 7.21 6.84 | 3.80 | |
| 7b | $Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)(TCNE)I$ | 2200 s | 2219 sh | 7.17 s | 2.38 | |
| 8 | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(FN)]ClO_4$[i] | 2198 w, 2155 s | 2220 sh | 6.92 s | 3.85 | |
| 9a | $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_2(FN)]ClO_4$[j] | 2188 s, 2134 w | 2212 m | 7.05 6.87 | 3.80 | 3.80 t |
| 9b | $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_2(FN)]ClO_4\cdot FN$[k] | 2191 s, 2139 w | 2214 m | 7.22 7.02 | 2.36 | 3.80 t |
| 10a | $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(FN)I$[l] | 2181 s, 2130 m | 2211 m | 7.17 6.84 | 3.81 | |
| 10b | $Rh(p\text{-}CH_3C_6H_4NC)_2(P(OPh)_3)(FN)I$[m] | 2182 s, 2131 m | 2214 m | 7.12 s | 2.34 | |

[a] Measured in $CH_2Cl_2$. Key: s, strong; m, medium; w, weak; sh, shoulder. [b] Isocyanide vibration. [c] Cyanoolefin vibration. [d] Obscured by the strong $\nu$(NC) band of the isocyanides. [e] Measured in $CH_2Cl_2$ at 25°, unless otherwise noted. [f] $A_2B_2$ type quartet with a coupling constant of about 9 Hz, unless otherwise noted; s = singlet. [g] Key: s, singlet; br, broad; d, doublet with a coupling constant of about 12 Hz; t, an intermediate case of a virtual coupling pattern with a coupling constant of about 12 Hz. [h] Obscured by $P(OPh)_3$ signals. [i] FN proton signal could not be detected. [j] $\delta$(FN) 3.70 (br) at 25° and 3.21 (quintet) ppm at −55°. [k] FN protons could not be detected at 25°. $\delta$(coordinated FN) 3.26 (quintet) and $\delta$(free FN) 6.34 (s) ppm at −52°. [l] $\delta$(FN) 3.32 (br) at 25° and around 3.1 and 2.2 ppm at −55° as an overlap of two AB type quartets. [m] $\delta$(FN) 3.84 (br) at 25° and around 3.1 and 2.3 ppm at −60° as an overlap of two AB type quartets.

was filtered and recrystallized from $CH_2Cl_2$–petroleum ether to give orange needles of **7a** (27 mg, 41%).

**Preparation of the FN Complexes. Bis(*p*-methoxyphenyl isocyanide)bis(triphenyl phosphite)(fumaronitrile)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(FN)]ClO_4$ (8).** A solution of FN (86 mg, 1.1 mmol) in $CH_2Cl_2$ (2 ml) was added to **1a** (300 mg, 0.27 mmol) in $CH_2Cl_2$ (5 ml) and the solution was stirred for 30 min. Concentration under reduced pressure gave a product which was filtered and recrystallized from $CH_2Cl_2$–petroleum ether to afford pale yellow crystals of **8** (270 mg, 84%).

**Bis(*p*-methoxyphenyl isocyanide)bis(dimethyl phenylphosphonite)(fumaronitrile)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_2(FN)]ClO_4$ (9a).** The product obtained from a reaction of **2a** (220 mg, 0.22 mmol) with FN (60 mg, 0.8 mmol) was recrystallized from $CH_2Cl_2$–petroleum ether to afford white crystals of **9a** (180 mg, 94%).

**Iodobis(*p*-methoxyphenyl isocyanide)(triphenyl phosphite)(fumaronitrile)rhodium, $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(FN)I$ (10a).** To a solution of **1a** (140 mg, 0.13 mmol) in $CH_2Cl_2$ (5 ml) was added a solution of FN (30 mg, 0.4 mmol) in $CH_2Cl_2$ (2 ml) and then NaI (20 mg, 0.13 mmol) in $C_2H_5OH$ (2 ml). The solution was stirred at room temperature for 2 hr, refluxed for 1 hr, cooled, and concentrated under reduced pressure to precipitate a product, which was filtered and recrystallized from $CH_2Cl_2$–petroleum ether to give yellow needles of **10a** (75 mg, 70%).

**Reactions of $[Rh(RNC)_2(PPh_2(OMe))_3]ClO_4$ (3) with FN (R = *p*-$CH_3OC_6H_4$ or *p*-$CH_3C_6H_4$).** Reactions between the rhodium substrates and FN were carried out in manners similar to that described for **9a**, resulting in recovery of the starting materials.

**The Measurements of the Formation Constants of 4a and 8.** The formation constants were determined spectrophotometrically by using a Hitachi 124 spectrophotometer; the absorbance at 397 m$\mu$ was measured for $CH_3CN$ solutions of **1a** (2.50 × $10^{-4}$ *M*) containing various amounts of TCNE (0–6.3 × $10^{-4}$ *M*) or FN (0–5 × $10^{-1}$

*M*). The formation constants were calculated by the methods of Rose and Drago[8] and Ketelaar, *et al.*,[9] for the TCNE and FN complexes, respectively.

## Results and Discussion

**Preparation.** The starting complexes **1** are cleanly prepared by reactions of $[Rh(1,5\text{-}C_8H_{12})(P(OPh)_3)_2]ClO_4$ with 2 molar equiv of the appropriate isocyanides. Preparation of **1a** *via* *trans*-$RhCl(CO)(P(OPh)_3)_2$ was described in literature.[10] Our methods seem to be generally applicable for the synthesis of rhodium cationic complexes containing both isocyanides and ligands of another kind. In fact, **2** and **3** are similarly prepared from $[Rh(1,5\text{-}C_8H_{12})L_3]ClO_4$ (L = $PPh(OMe)_2$ or $PPh_2(OMe)$). The TCNE complexes are prepard from an addition reaction of **1** or from phosphorus ligand substitution reactions of **2** and **3** by an equimolar amount of TCNE. The FN complexes are prepared in a similar manner to that of the TNCE complexes using 4 molar equiv of FN; however, reactions of **3** even with 4 molar equiv of FN led only to recovery of the starting materials. The TCNE complexes are generally much more stable than the FN ones against dissociation in solution; the formation constants of the following equilibrium are $4.0 \times 10^3$ and 1.4 $M^{-1}$ for the TCNE and FN complexes in $CH_3CN$ at 25°, respectively.

$$[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4 + \text{cyanoolefin} \rightleftharpoons [Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(\text{cyanoolefin})]ClO_4$$

**1** reacts with TCNE and FN in the presence of NaI to afford neutral complexes **7** and **10** with dissociation of one molecule of $P(OPh)_3$. This result may be analogous to the reaction of $[Rh(RNC)_2(PPh_3)_2]I$ (R = $CH_3$ or $p\text{-}CH_3OC_6H_4$) with cyanoolefins, which was previously reported by us.[2] The starting complexes **1**, **2**, and **3**, are yellow and the cyanoolefin complexes **4**–**10** are almost colorless, yellow, or orange. All these complexes in the solid state are stable in the air. In the ir spectra of the closely related complexes (**1**, **4**, and **8**; **2**, **5**, and **9**; **3** and **6**), the $\nu$(NC) frequency decreases in the order of TCNE > FN > the parent complexes. Moreover, the $\delta$ values of the isocyanide and *P*-OMe proton signals decrease in the opposite order (Table II). These two features suggest that the extent of charge transfer from the the rhodium atom to the ligands decreases in the order of TCNE > FN > phosphorus ligands.

**The Starting Complexes 1–3.** The ir spectra of **1** in $CH_2Cl_2$ show only one strong $\nu$(NC) band and the pmr spectra show only one set of an $A_2B_2$ type quartet and a singlet for the phenyl ring and the $CH_3O$ protons of the isocyanides, respectively (Table II). These two results are consistent with square-planar configurations with the two mutually trans isocyanides for **1**.

The ir spectrum of **3a** in $CH_2Cl_2$ shows a strong $\nu$(NC) band and a weak shoulder. A shoulder is also seen in Nujol mulls. This result may be interpreted by assuming a trigonal bipyramid with the trans isocyanides deviating slightly from the axial positions. The temperature-dependent pmr spectra of the *P*-OMe protons of **3a** are shown in Figure 1. The broad signal at 25° becomes broader as the temperature is lowered and begins to split around −5°; at −30° a clear quartet can be seen. In view of a slight temperature dependence of the chemical shifts of the ligand protons, the spectral change between +25° and −5° may be due to a slight dissociative exchange of $PPh_2(OMe)$. Actually, in the variable-temperature pmr spectra of **3a** in the presence of 3 molar equiv of $PPh_2(OMe)$ a broad singlet appears at an averaged chemical shift between those of the free and coordinated $PPh_2(OMe)$ at 25°; while below 5° both of the signals are clearly distinguished and at −20° the signals are a doublet and a quartet as seen in the spectrum of **3a** only. The signal of **3a** is practically unchanged down to −55°; however, at −80° it is less resolved. In a 1:5 mixture of $CH_2Cl_2$ and $CHClF_2$ at −84° the signal is rather well resolved, although at −96° it is again less resolved. Since the low-temperature limiting spectrum could not be obtained, the broadening could be caused by a dynamic phenomenon as well as by viscosity or other difficulties encountered in nmr meausrements. Thus, any definite conclusion about the dynamic behavior of **3a** will be premature. **2a**, **2b**, and **3b** behave essentially in a similar manner.

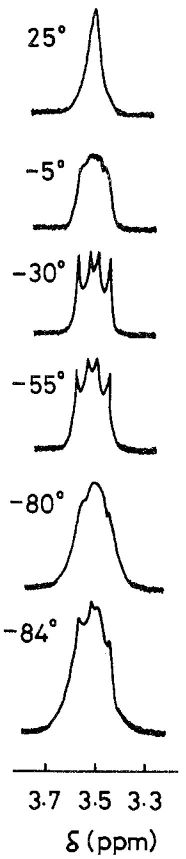

Figure 1. Temperature-dependent pmr spectra of *P*-OMe protons of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_2(OMe))_3]ClO_4$ (3a) in $CH_2Cl_2$ (above −80°) and in a 1:5 mixture of $CH_2Cl_2$ and $CHClF_2$ (−84°).

**The TCNE Complexes 4–7.** The ir spectrum of **4a** in $CH_2Cl_2$ shows a strong $\nu$(NC) band at 2213 $cm^{-1}$ and a weak one at 2153 $cm^{-1}$. The latter corresponds to that of the starting complex **1a**, indicating a slight dissociation of TCNE in solution. This result is conceivable in view of the formation constants of **4a** ($4.0 \times 10^3$ *M*). The 2213-$cm^{-1}$ band can be assigned to the undissociated adduct judging from the magnitude of its frequency shift. Appearance of the only one $\nu$(NC) band in **4a** will suggest the trans isocyanides. **4b** may have a similar configuration.

The ir spectrum of **6a** shows a strong $\nu$(NC) band and a medium $\nu$(CN) band of the coordinated TCNE. The pmr spectrum of **6a** shows an $A_2B_2$ type quartet and a sharp singlet for the phenyl ring and the $CH_3O$ protons of the isocyanides and a doublet for the MeO protons of $PPh_2(OMe)$. Thus, **6a** is suggested to take a trigonal-bipyramidal form with the axial isocyanides and equatorial $PPh_2(OMe)$. Little temperature dependence of the signal pattern over a wide temperature range (between +40 and −55°) reveals the presence of a rigidly bonded TCNE. **5a**, **5b**, and **6b** show essentially similar spectroscopic data and may have an analogous configuration.

**7** is also suggested to have a trigonal-bipyramidal form with the axial isocyanides and a rigidly bonded TCNE on the basis of the data (Tables I and II).

Recently we have reported that TCNE is nonrigid in $[Rh(RNC)_4(TCNE)]ClO_4$ but rigid in $[Rh(RNC)_2$-

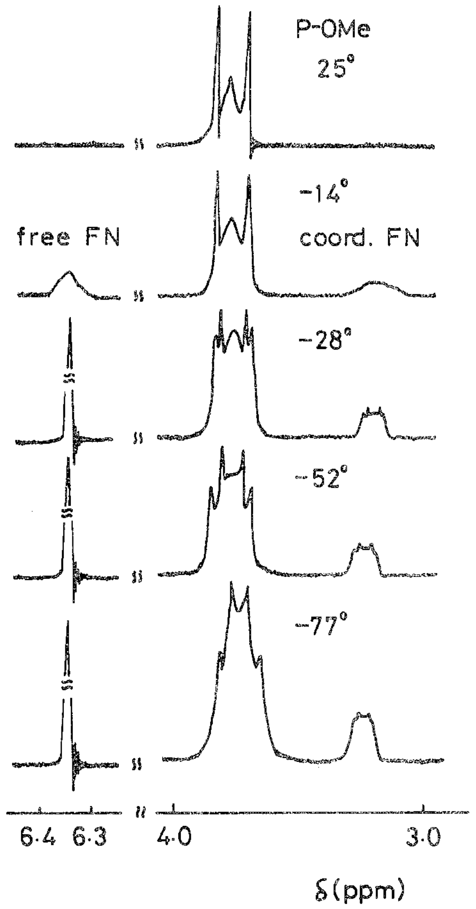

**Figure 2.** Temperature-dependent pmr spectra of $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_2(FN)]ClO_4\cdot FN$ (**9b**) in $CH_2Cl_2$. Only the signals for the free and coordinated FN and *P*-OMe protons of $PPh(OMe)_2$ are shown.

$(PPh_3)_2(TCNE)]ClO_4$ (R = *p*-$CH_3OC_6H_4$, etc.)[2a] and interpreted the difference in terms of the stronger electron-donating property of $PPh_3$ than that of the isocyanide ligands. On the other hand, the present results indicate that TCNE is all rigid in $[Rh(RNC)_2P_2(TCNE)]ClO_4$ (P = $P(OPh)_3$ (**4**), $PPh(OMe)_2$ (**5**), and $PPh_2(OMe)$ (**6**); R = *p*-$CH_3OC_6H_4$ (**a**) and *p*-$CH_3C_6H_4$ (**b**)). The electronic property of $P(OPh)_3$ is suggesteed to resemble that of isocyanides[4] and π-acceptor ability is thought to decrease in the order of $PPh(OMe)_2 > P(OPh)_3$.[11] Thus, it is considered that occurrence of the rigid complexes, **4**, **5**, and probably **6**, may be related to the large steric hindrance rather than to the electronic effects of the phospshorus ligands.

**The FN Complexes 8–10.** The ir spectrum of **8** in $CH_2Cl_2$ shows a medium ν(NC) band at 2198 $cm^{-1}$ and a strong one at 2155 $cm^{-1}$; the latter frequency is exactly the same as that of the starting complex **1a**, indicating an extensive dissociation of FN. This is in accord with the formation constant of **8** (1.4 $M^{-1}$ in $CH_3CN$ at 25°).

**9b** exhibits a medium ν(CN) band of the coordinated FN, a strong ν(NC) band assignable to **9b**, and a weak ν(NC) band which may be due to the four-coordinated species $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_2]ClO_4$ upon dissociation of FN from **9b**. The undissociated **9b** may have trans isocyanides. The temperature-dependent pmr spectra of **9b** are illustrated in Figure 2. The crystal sample of **9b** contains two molecules of FN: the coordinated one and free one probably packed in the crystal lattice. The spectrum at 25° shows no signal assignable to FN, indicating a rapid exchange between the free and coordinated FN molecules. At −14° there appear two broad signals assignable to the free and coordinated FN at δ 6.32 and 3.21 ppm, respectively. These signals become sharp with the constant chemical shift values, as the temperature is further lowered, indicating negligible exchange between the two kinds of FN at lower temperatures than −14° on the nmr time scale.

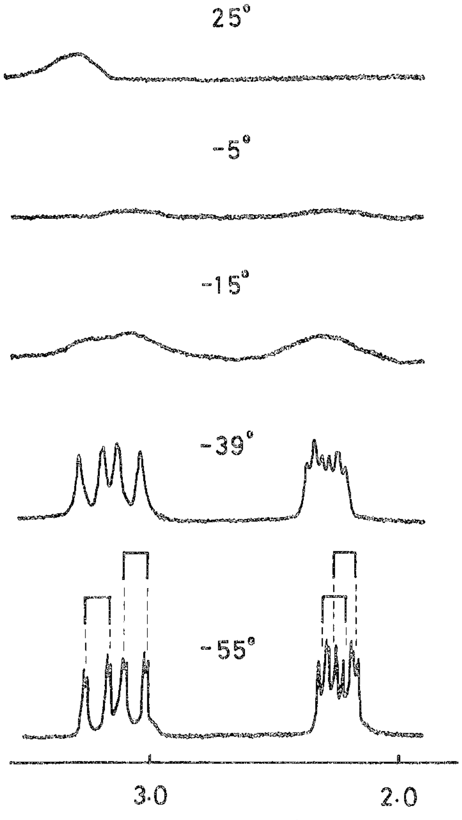

**Figure 3.** Temperature-dependent pmr spectra of FN in $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(FN)I$ (**10a**) in $CH_2Cl_2$.

The *P*-OMe signal of **9b** shows an interesting change of a virtual coupling pattern. Thus, the signal at 25° corresponds to a medium P–Rh–P coupling arising from the mutually trans $PPh(OMe)_2$ as in the case of $[Ir(CO)_3(PMe_2Ph)_2]^+$.[12] At −14° the signal becomes a little broader, and at −28° a symmetrical quintet can be seen, which is analogous to that of $[Pd(allyl)(PMe_2Ph)_2]^+$.[13] At −52° the broad component at the center of the signal collapses and finally a symmetrical quartet appears at −77°, which is very similar to the *P*-OMe signal of the starting complex **2b** at low temperature. The signal of the coordinated FN shows essentially an analogous change of a virtual coupling pattern; the *P*-OMe signal corresponds to the spin system $[M[AX_6]_2]$ ($D_{3h}$, rotation) and that of FN to $[M[AX]_2]$ ($C_{2v}$).[14] These signal changes may be consistent with the following interpretation. In the temperature region between +25 and −14° the P–Rh–P skeleton experiences an average magnetic environment between a bent skeleton in **9b** and an almost linear skeleton in the four-coordinated species $[Rh(p\text{-}CH_3C_6H_4NC)_2(PPh(OMe)_2)_2]ClO_4$ upon dissociation of the coordinated FN from **9b**. Below −28° the intramolecular interaction between FN and the rhodium atom may become stronger, resulting in the further bending of the P–Rh–P skeleton and thus in a weaker P–Rh–P coupling.

The ir spectrum of **10a** shows a medium ν(CN) band of the coordinated FN, a strong ν(NC) band of **10a**, and a medium ν(NC) band which may be due to the four-coordinated species $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)I$ arising from the dissociation of FN. Actually molecular weights of **10** are slightly smaller than the calculated monomer values (Table I). The

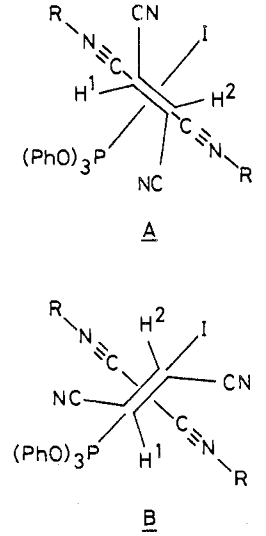

**Figure 4.** Isomeric forms of Rh(RNC)$_2$(P(OPh)$_3$)(FN)I (**10**) (viewed from the FN side). The rhodium atom is omitted for clarity.

temperature-dependent pmr spectra of FN of **10a** are shown in Figure 3. The broad singlet at 25° at $\delta$ 3.3 ppm is more broadened and shifted to the higher field as the temperature is lowered and apparently disappears at −5°. At −15° the FN signal appears as two broad components centered around $\delta$ 3.1 and 2.2 ppm. On further cooling the components become sharper without changing the chemical shift and the signal at −39° can be explained as a superposition of two AB type quartets with the coupling constants of 9.4 Hz (Figure 3). At −55° each component of the quartets is further split into a doublet; the lower field components have the coupling constants of 1.5 Hz and the higher field ones the values of 3.6 and 4.2 Hz. These pmr features may be interpreted as follows. In the temperature range between +25 and −5° a fast exchange between the free and coordinated FN is occuring. Below −15° the amount of free FN is negligible on the nmr time scale and the signal change will be due to the restricted rotation of FN in a time-averaged square pyramid. This topic has been discussed in detail in the compounds [Rh(RNC)$_4$(TCNE)]ClO$_4$, Rh(RNC)$_2$(PPh$_3$)(FN)I, and [Rh(RNC)$_2$(PPh$_3$)$_2$(FN)]ClO$_4$ in our previous paper.[2] When the rotation of FN is inhibited, there will be two isomeric forms of **10a** (A and B) as depicted in Figure 4. Each of them has a nonsuperimposable mirror image, resulting in four different isomers altogether. In each of A and B the H$^1$ and H$^2$ protons of FN are in different magnetic environments, resulting in an AB type quartet. Since there appears an overlap of two quartets, both of A and B will exist.

**Registry No.** **1a**, 53992-55-5; **1b**, 53992-57-7; **2a**, 53992-59-9; **2b**, 53992-61-3; **3a**, 53992-63-5; **3b**, 53992-65-7; **4a**, 53992-67-9; **4b**, 53992-69-1; **5a**, 53992-71-5; **5b**, 53992-73-7; **6a**, 53992-75-9; **6b**, 53992-77-1; **7a**, 53992-78-2; **7b**, 53992-79-3; **8**, 53992-81-7; **9a**, 54020-29-0; **9b**, 54020-31-4; **10a**, 53992-82-8; **10b**, 53992-83-9; [Rh(1,5-C$_8$H$_{12}$)(P(OPh)$_3$)$_2$]ClO$_4$, 32799-69-2; [Rh(1,5-C$_8$H$_{12}$)(PPh(OMe)$_2$)$_3$]ClO$_4$, 53992-85-1.

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# Properties of Ni(DPG)$_2$X (DPG = Diphenylglyoximato; X = Br, I) in the Presence of Donor Molecules and in the Solid

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Bis(diphenylglyoximato)nickel(II), Ni(DPG)$_2$, is oxidized by iodine and bromine in the presence of nitrogen donors to form nickel(III) complexes. Results from epr spectral studies of [Ni(DPG)$_2$(py)$_2$]I are compared with the results from the isoelectronic species Co(DPG)$_2$(py)$_2$. Both complexes have a $(d_{xz}, d_{yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. Analysis of the nitrogen-14 hyperfine coupling from pyridine in the $g_\parallel$ and $g_\perp$ regions for these complexes indicates that the $\sigma$-donor orbital for coordinated pyridine is essentially an sp$^2$ hybrid. Electronic and epr spectra for samples of Ni(DPG)$_2$ X (X = Br, I) in the solid are reported. The observed epr signal is assigned to an imperfection in the metal chains, resulting in a [Ni$^{\text{II}}$(DPG)$_2$]$^+$ site.

## Introduction

Planar nickel(II) chelate complexes are known to frequently undergo one-electron oxidations at either the Ni(II) or chelate ligand sites.[1-3] Epr spectra are diagnostic for the presence of Ni(III) or oxidized ligand.[1,2] Bis(diphenylglyoximato)metal(II) (metal = nickel, palladium) react with I$_2$ and Br$_2$ to form species with the stoichiometry M(DPG)$_2$ X (X = Br, I).[4] The parent Ni(DPG)$_2$ complex occurs with a columnar structure involving a chain of M sites with M–M distances of 3.52 Å.[5] Reaction with halogens is thought to occur with retention of this general structural feature and a shortening of the average M–M distance to 3.27 Å[6] although the X-ray structure has not been completed.

Conductivity properties associated with pseudo one-dimensional systems have promoted a resurgence of interest in materials with structural features of this type.[7,8] This paper reports on the interaction of donor molecules such as pyridine with Ni(DPG)$_2$X to form nickel(III) species of the form [Ni(DPG)$_2$(py)$_2$]$^+$X$^-$ along with some properties of solid Ni(DPG)$_2$X. Spectroscopic and bonding properties of the