and which by 12. The signal of the bridging methine proton in $[Ph_2P(O)CHRPPh_2Me]PF_6$ is weak and the complex signal was not analyzed.

Registry No. $Ph_2P(O)CH_2Li$, 23182-99-2; $Ph_2P(O)CH(CH_3)Li$, 25082-62-6; $Ph_2P(O)CH$(*n*-Pr)Li, 53849-91-5; Ph_2PCl, 1079-66-9; PhEtPCl, 15849-83-9; $Ph_2P(O)CH_2PPh_2$, 23176-18-3; $Ph_2P(O)CH(CH_3)PPh_2$, 53849-92-6; $Ph_2P(O)CH$(*n*-Pr)PPh_2, 53849-93-7; $[Ph_2P(O)CH_2PPh_2CH_3]PF_6$, 53849-73-3; $[Ph_2P(O)CH(CH_3)PPh_2CH_3]PF_6$, 53849-41-5; $[Ph_2P(O)CH$(*n*-Pr)$PPh_2CH_3]PF_6$, 53849-43-7; $[Ph_2P(O)CH$(*n*-Pr)$PPh_2]Cr(CO)_4$, 53849-44-8; $[Ph_2P(O)CH$(*n*-Pr)$PPh_2]Mo(CO)_4$, 53849-45-9; $[Ph_2P(O)CH$(*n*-Pr)$PPh_2]W(CO)_4$, 53849-46-0; $[Ph_2P(O)CH_2PPh_2]HgCl_2$, 53849-47-1; $[Ph_2P(O)CH_2PPh_2]HgBr_2$, 53849-48-2; $[Ph_2P(O)CH_2PPh_2]CdBr_2$, 53849-49-3; $[Ph_2P(O)CH$(*n*-Pr)$PPh_2]CdBr_2$, 53849-50-6; $[Ph_2P(O)CH$(*n*-Pr)$PPh_2]HgCl_2$, 53849-51-7; $[Ph_2P(O)CH$(*n*-Pr)$PPh_2]HgBr_2$, 53849-52-8; $Ph_2P(O)CH_2P(O)PhEt$, 17045-59-9; $Ph_2P(O)CH(CH_3)P(O)Ph_2$, 53849-94-8.

References and Notes

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Cyanide, Isocyanide, and Nitrile Derivatives of Cyclopentadienyliron. Interaction of Chiral Metal Complexes with an Optically Active Shift Reagent

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The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]I$ with excess cyanide yields $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$. Ethylation with Et_3OPF_6 yields $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6$. This isocyanide compound does not react with a variety of nucleophiles to yield addition products but was clearly shown to be an isocyanide compound by comparison with $[(\eta^5\text{-}C_5H_5)Fe(CO)(NCMe)(PPh_3)]BF_4$. The reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ with KCN yields $K[(\eta^5\text{-}C_5H_5)Fe(CN)_2(PPh_3)]$. This reaction is contrasted by the reaction of excess KCN with $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ in ethanol to yield $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$ and in ethanol–water to yield $K[(\eta^5\text{-}C_5H_5)Fe(CO)(CN)_2]$. The conversion of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$ to $K[(\eta^5\text{-}C_5H_5)Fe(CO)(CN)_2]$ in ethanol–water with KCN showed that the latter reaction takes place in two steps. The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}(CH_2)_nCN)$ ($n = 1, 2$) were prepared respectively by the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ with $LiCH_2CN$ ($n = 1$) and the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}C_2H_4)]BF_4$ with KCN ($n = 2$). The ^1H and ^{13}C nmr of these two new complexes and $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$, complexes containing a chiral metal center, in the presence of various concentrations of Yb-Optishift I[1] was measured. Resolution of the enantiotopic protons of the $\eta^5\text{-}C_5H_5$ was observed for $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CN)$ whereas none was observed for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CH_2CN)$. Very little resolution was observed for any resonances in the ^{13}C spectra.

Introduction

The chemistry of cyanide and isocyanide ligands, formally isoelectronic to carbon monoxide, has not been explored in as great detail as the chemistry of the carbonyl ligand. Because these ligands offer considerable potential synthetic utility, recent interest in the synthesis and reactivity of transition metal organometallic cyanide and isocyanide compounds has been quite high. The main emphasis of this work, especially with isocyanides, has been on nickel, palladium, and platinum compounds[2,3] although research on other transition metals has been carried out.[4] Of particular interest has been the reactivity of the isocyanide ligand toward nucleophilic reagents.[2b,3b,4b] Reactions with hydroxide, sulfides, and amides yield carboxamido, thiocarboxamido, and amidinium metal complexes, respectively.[2b] Reactions with amines and alcohols yield carbene complexes.[3b,4b] This reactivity is analogous to nucleophilic reactions of the carbon of a metal carbonyl.[5,6]

This report describes the reaction of cyanide with $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]I$ and compares it to the reaction of cyanide with $(\eta^5\text{-}C_5H_5)Fe$-

$(CO)_2I$. The phosphine ligand places considerably more electron density on the metal center than a carbonyl, changing the chemistry drastically. Also, the preparation and reactivity of the isocyanide compound $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6$ (**1**) is described. These particular compounds were chosen for study because the iron in compounds like **1** is chiral.[7] It was hoped that the reaction chemistry of these species, especially **1**, would lead to new compounds in which the metal center could be easily resolved. In addition, the preparation of two alkyl cyanides, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CN)$ (**2**) and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CH_2CN)$ (**3**), is described. The ^1H and ^{13}C nmr spectra of these two compounds and $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$ (**4**) in the presence of Yb-Optishift I[1] is reported. Marks, *et al.*,[8] have observed a significant shift of the $\eta^5\text{-}C_5H_5$ resonance in $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CN)$ in the presence of lanthanide shift reagents indicating that by using an optically active shift reagent enantiomeric composition of chiral metal complexes could be determined in a manner similar to that recently applied to organic compounds.[9]

Experimental Section

General Data. All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen using solvents that were purified and degassed before use. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer. Proton nmr spectra were recorded on a Varian A-60 spectrometer. Carbon-13 nmr spectra were recorded on a Varian CFT-20 spectrometer using CH_2Cl_2 as the solvent and internal standard. Chemical shifts are reported *vs.* TMS assigning the CH_2Cl_2 resonance to be at 54.0 ppm and all spectra were run with ^1H decoupling. Mass spectra were measured, at 70 eV, on a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Melting and decomposition points were determined in sealed capillaries and are uncorrected. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]I$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ used in this study were prepared as outlined by Treichel, *et al.*[10]

Cyano(η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iron(II) (4). A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]I$ (10 g, 17.7 mmol) and NaCN (2.5 g, 51.0 mmol) was allowed to react in refluxing absolute ethanol (400 ml) with stirring for 24 hr. The solvent was evaporated, the residue extracted with boiling toluene (250 ml), and this solution filtered hot. Slow cooling of the filtrate to 0° yielded small orange crystals that were collected, washed with benzene (30 ml), and dried *in vacuo* (5.2 g, 67.3%), mp 228–230°. *Anal.* Calcd for $C_{25}H_{20}FeNOP$: C, 68.67; H, 4.58; N, 3.20. Found: C, 68.77; H, 4.76; N, 3.05. ^1H nmr spectrum (δ in $CDCl_3$): 4.57 (5, doublet, J = 1.2 Hz, $\eta^5\text{-}C_5H_5$), 7.40 (15, broad, PPh_3). Ir spectrum (cm^{-1} in benzene): ν(CO) 1959 (vs), ν(CN) 2099 (m). Mass spectrum: 437 (molecular ion), 409, 383, 262 (PPh_3). ^{13}C nmr spectrum: 218.21 (doublet, J = 28.3 Hz, CO), 135.09 (doublet, J = 46.3 Hz, P-bound phenyl carbons), 133.34 (doublet, J = 9.9 Hz, meta phenyl carbons), 130.55 (doublet, J = 2.0 Hz, para phenyl carbons), 128.44 (doublet, J = 10.0 Hz, ortho phenyl carbons), 84.27 (singlet, $\eta^5\text{-}C_5H_5$); the cyano carbon was not located and is believed to lie under the phenyl resonances.

(η^5-Cyclopentadienyl)carbonyl(ethyl isocyanide)triphenylphosphineiron(II) Hexafluorophosphate (1). A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$ (8.0 g, 18.3 mmol) and Et_3OPF_6 (4.8 g, 19.3 mmol) was stirred in CH_2Cl_2 (100 ml) for 0.5 hr. The solvent was evaporated, the resulting orange oil dissolved in boiling ethanol (400 ml), and this solution filtered hot. Cooling to −15° yielded yellow-orange needles that were collected and dried (100° (0.001mm)). These needles contained 0.5 equiv of ethanol of crystallization (11.2 g, 96.6%), mp 177–178°. *Anal.* Calcd for $C_{27}H_{25}F_6FeNOP_2\cdot 0.5C_2H_6O$: C, 53.01; H, 4.42; F, 17.99; N, 2.21. Found: C, 52.94; H, 4.17; F, 18.32; N, 2.19. ^1H nmr spectrum (δ in $CDCl_3$): 0.95 (3, triplet, J = 7.35 Hz, NCH_2CH_3), 1.20 (1.5, triplet, J = 7.2 Hz, 0.5 OCH_2CH_3), 3.61 (3, multiplet, NCH_2, 0.5 OCH_2), 4.89 (5, doublet, J = 1.2 Hz, $\eta^5\text{-}C_5H_5$), 7.47 (15, broad with upfield shoulder, PPh_3). Careful integration at 100 MHz of the 0.95 and 1.20 peaks yielded exactly a ratio of 2:1. Ir spectrum (cm^{-1}): ν(CO) 1980 ($CHCl_3$), 1984 (vs) (Nujol mull), ν(CN) 2179 ($CHCl_3$), 2185 (s) (Nujol mull), ν(O–H) 3570 (Nujol mull), ν(P–F) 830–870 (broad double band) (Nujol mull). ^{13}C nmr spectrum: 213.78 (doublet, J = 26 Hz, CO), 132.39 (doublet, J = 10 Hz, meta phenyl carbons), 132.15 (doublet, J = 48.7 Hz, P-bound phenyl carbons), 131.20 (singlet, para phenyl carbons), 128.84 (doublet, J = 10.1 Hz, ortho phenyl carbons), 85.33 (singlet, $\eta^5\text{-}C_5H_5$), 57.79 (singlet, OCH_2), 40.65 (singlet, $N\text{-}CH_2$), 18.11 (singlet OCH_2CH_3), 13.50 (singlet, NCH_2CH_3).

Potassium Dicyano(η^5-cyclopentadienyl)triphenylphosphineferrate(II) (7). To a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ (3.0 g, 5.6 mmol) and KCN (1.5 g, 23.0 mmol) was added absolute ethanol (150 ml) and the resulting suspension was heated to reflux. Over a 1-hr period, the color of the solution changed from green to yellow. The reflux was stopped and the ethanol evaporated. The residue was extracted with boiling hexane (100 ml) and the solution was decanted. Evaporation of the hexane yielded triphenylphosphine (0.62 g, 44.6%). The residue remaining after the hexane extraction was dissolved with boiling CH_2Cl_2 (80 ml); this solution, filtered hot and cooled slowly to −20°, yielded over 2 days small orange needles. These were collected, washed with cold CH_2Cl_2 (3 ml), and dried *in vacuo* (0.76 g, 30%), dec pt 160–162°. These crystals were shown to contain 1 equiv of water which must have been introduced by the KCN that was weighed in air. *Anal.* Calcd for $C_{25}H_{20}FeKN_2P\cdot H_2O$: C, 60.86; H, 4.46; Fe, 11.33; K, 7.93; N, 5.68; O, 3.25; P, 6.29. Found: C, 61.16; H, 4.81; Fe, 11.10; K, 7.83; N, 5.62; O, 3.17 (by difference); P, 6.31. ^1H nmr spectrum (δ in DMSO-d_6): 3.28 (2, singlet, H_2O), 3.78 (5, doublet, J = 1.3 Hz, $\eta^5\text{-}C_5H_5$), 7.37 (15, broad with downfield shoulder, PPh_3). Ir spectrum (cm^{-1}): ν(CN) 2033 (s), 2047 (s) (Nujol mull), 2031, 2048 (CH_2Cl_2 solution).

A reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ and KCN exactly the same as that described above was carried out. The crude reaction residue was extracted with boiling hexane (100 ml) to remove triphenylphosphine and the remaining red oil was extracted with toluene (6 ml) and chromatographed (3 × 30 cm alumina column). Elution with benzene–acetone (1:1 v/v) developed a weak red band that was identified by infrared analysis as $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$ (*ca.* 0.05 g) by comparison with an authentic sample.

(η^5-Cyclopentadienyl)carbonyl(acetonitrile)triphenylphosphineiron(II) Tetrafluoroborate (11). Acetonitrile (25 ml) was added to a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ (3.0 g, 5.6 mmol) and $AgBF_4$ (1.15 g, 5.9 mmol). The green solution became red in 5 min. After 0.5 hr, the excess acetonitrile was evaporated, the residue dissolved in a CH_2Cl_2–benzene mixture (1:4 v/v, 140 ml), and this solution filtered hot. Cooling to 0° yielded a red powder that was collected, washed with benzene (two 20-ml portions), and dried *in vacuo* (2.7 g, 94.5%), mp 168–169°. *Anal.* Calcd for $C_{26}H_{23}BF_4FeNOP$: C, 57.92; H, 4.27; N, 2.60; F, 14.11. Found: C, 58.44; H, 4.51; N, 2.45; F, 13.85. The spectral properties matched those already reported by Treichel, *et al.*[10] This compound decomposes to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]BF_4$ rapidly in boiling ethanol. It does not react with KCN at room temperature and decomposes to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]BF_4$ in refluxing ethanol in the presence of KCN.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with KCN in Ethanol and Ethanol–Water. The reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and KCN in refluxing absolute ethanol carried out in exactly the same manner as described above for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ yielded $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$. A similar reaction in refluxing ethanol–water (4:1 v/v) yielded $K[(\eta^5\text{-}C_5H_5Fe(CO)(CN)_2]$. This chemistry parallels that of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ reported earlier by Coffey.[11]

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CN)$ with KCN in Ethanol–Water. A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CN)$ (0.3 g, 1.5 mmol) and KCN (0.25 g, 3.8 mmol) was refluxed in ethanol–water (4:1 v/v, 100 ml) for 11 hr. The solvent was evaporated and the residue extracted with ethanol (40 ml). This solution was filtered, concentrated to 15 ml at 60°, and cooled slowly to room temperature. The resulting orange crystals were collected, dried, and recrystallized from ethanol (15 ml) to yield $K[(\eta^5\text{-}C_5H_5)Fe(CO)(CN)_2]$ (0.22 g, 61%).

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6$ with Various Nucleophiles. 1. Sodium Ethoxide. To an ethanol (18 ml) solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6$ (0.8 g, 1.15 mmol) was added NaOEt (2.17 mmol) in ethanol (25 ml). No reaction took place at room temperature, but heating at 65° for 6 hr caused the color of the solution to change from yellow to deep red. The solvent was removed, and the residue was dissolved in benzene (4 ml) and chromatographed (alumina, 3 × 10 cm). Elution with benzene yielded a red band that proved to be $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ by comparison with an authentic sample.

2. Potassium Cyanide. A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}$

bach,[14] and (η^5-C_5H_5)Fe(CO)(PPh_3)I (10 g, 18.6 mmol) was added in one portion. The solution was warmed to room temperature and stirred overnight. The solvent was evaporated, the residue was extracted with CH_2Cl_2 (200 ml), and the solution was filtered hot. This solution was reduced to 25 ml and chromatographed (5 × 30 cm alumina column). Elution with CH_2Cl_2 developed four bands. The first of these was ferrocene (*ca.* 1.0 g), the second was trace amounts of starting reactant, and the third was [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ (*ca.* 0.3 g). An orange band still remained at the top of the column that was eluted with acetone–CH_2Cl_2 (1:3 v/v). The solvent was evaporated from this band and the residue recrystallized from benzene–hexane (45 ml, 1:2 v/v) to yield red crystals (0.85 g, 10%), mp 164–165°. *Anal.* Calcd for $C_{26}H_{22}FeNOP$: C, 69.20; H, 4.87; N, 3.10. Found: C, 69.31; H, 4.92; N, 3.15. ^{1}H nmr (δ in $CDCl_3$): 0.61 and 0.72 (2, CH_2CN), 4.40 (5, doublet, J = 1.2 Hz, η^5-C_5H_5), 7.33, 7.42 (15, PPh_3). Ir spectrum (cm^{-1}): ν(CO) 1930 (vs) (Kel-F mull), 1928 (benzene), ν(CN) 2188 (s) (Kel-F mull), 2190 (benzene). ^{13}C nmr spectrum: 221.37 (doublet, J = 30.2 Hz, CO), 135.35 (doublet, J = 41.3 Hz, P-bound phenyl carbons), 133.28 (doublet, J = 9.8 Hz, meta phenyl carbons), 130.16 (doublet, J = 2.1 Hz, para phenyl carbons), 128.50 (doublet, J = 9.6 Hz, ortho phenyl carbons), 85.11 (singlet, η^5-C_5H_5), 15.11 (doublet, J = 16.9 Hz, CH_2); the cyano carbon was not located and is believed to lie under the phenyl resonances.

(η^5-Cyclopentadienyl)carbonyl(2-cyanoethyl)(triphenylphosphine)iron(II) (3). A mixture of [(η^5-C_5H_5)Fe(CO)(PPh_3)(η^2-C_2H_4)]BF_4·C_6H_6 (3.0 g, 5.0 mmol) and KCN (1.0 g, 15.4 mmol) was stirred in absolute ethanol (150 ml) for 1 hr. The solvent was evaporated, the residue was extracted with benzene–hexane (75 ml, 1:4 v/v), and this solution was filtered hot. Slow cooling to 0° yielded large red crystals that were collected, washed with hexane, and dried *in vacuo* (1.8 g, 78%), mp 139–140°. *Anal.* Calcd for $C_{27}H_{24}FeNOP$: C, 69.70; H, 5.16; N, 3.01. Found: C, 69.74; H, 5.29; N, 2.95. ^{1}H nmr spectrum (δ in $CDCl_3$): two multiplets centered at 0.69 and 1.67 (2, $FeCH_2$), 2.24 (2, multiplet, CH_2CN), 4.28 (5, doublet, J = 1.3 Hz, η^5-C_5H_5), 7.40, 7.32 (15, PPh_3). Ir spectrum (cm^{-1}): ν(CO) 1897 (vs) (Kel-F mull), 1905 (benzene), ν(CN) 2223 (m) (Kel-F mull), 2226 (benzene). ^{13}C nmr spectrum: 222.58 (doublet, J = 31.9 Hz, CO), 136.30 (doublet, J = 40.7 Hz, P-bound phenyl carbons), 133.19 (doublet, J = 9.7 Hz, meta phenyl carbons), 129.87 (singlet, para phenyl carbons), 128.38 (doublet, J = 11.5 Hz, ortho phenyl carbons), 122.65 (doublet, J = 2.0 Hz, CN), 84.80 (singlet, η^5-C_5H_5), 24.0 (doublet, J = 3.6 Hz, CH_2CN), −2.67 (doublet, J = 20.1 Hz, $FeCH_2$).

Results and Discussion

Cyanide Reactions. The reaction of [(η^5-C_5H_5)Fe(CO)$_2$-(PPh_3)]I (**5**) with excess cyanide in refluxing ethanol yields (η^5-C_5H_5)Fe(CO)(CN)(PPh_3) (**4**).[15] This compound is stable to further substitution by cyanide. The same product might be expected from the reaction of (η^5-C_5H_5)Fe(CO)(PPh_3)I (**6**) with excess cyanide in refluxing ethanol, but this reaction yields only trace amounts (*ca.* 2%) of **4**. The main iron product is K[(η^5-C_5H_5)Fe(CN)$_2$(PPh_3)] (**7**) (30% yield) and, in addition, a 45% isolation of triphenylphosphine. There was no indication of the presence of any other iron-containing product. These reactions are contrasted by the reaction of (η^5-C_5H_5)Fe(CO)$_2$I (**8**) with excess KCN. In a reaction of **8** with KCN carried out exactly the same as the reaction of the phosphine derivative **6** in absolute ethanol (the KCN certainly introduces a small amount of H_2O) the product is (η^5-C_5H_5)Fe(CO)$_2$(CN) (**9**). The same reactants yield K[(η^5-C_5H_5)Fe(CO)(CN)$_2$] (**10**) if refluxed in ethanol–water (4:1 v/v). Although **9** does not react with KCN in ethanol, in ethanol–water it does react to yield **10**. This indicated that in the reaction of **8** with KCN in ethanol–water, **9** is formed initially and then reacts further to yield **10**.

Isocyanide Complex. The reaction of **4** with Et_3OPF_6 in CH_2Cl_2 yields [(η^5-C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6 (**1**) nearly quantitatively. This reaction is analogous to the alkylation of nitriles with trialkyloxonium salts to yield *N*-alkylnitrilium salts[17] and has been shown recently to take place for many platinum cyanide complexes.[2a] In contrast to *N*-alkylnitrilium and many transition metal isocyanide complexes, compound **1** does not react with alcohols. In fact, it was recrystallized from ethanol. It also did not react with excess (*S*)-(−)-α-phenylethylamine despite the recently reported addition of methylamine to [(η^5-C_5H_5)Fe(CO)(PPh_3)-(CNMe)]BPh_4.[18] Sodium ethoxide did not react with **1** to yield an addition product[2a] but yielded only [(η^5-C_5H_5)Fe-(CO)$_2$]$_2$. The isocyanide compound **1** reacts very slowly with the cyanide in refluxing ethanol to yield **4**. Only a small amount of **4** had formed in 8 hr in a reaction containing a considerable excess of cyanide. The reaction of **1** with excess $NaBH_4$ took place immediately at room temperature in THF and yielded (η^5-C_5H_5)Fe(CO)(PPh_3)H[12,13] in 48% yield. In contrast, **4** does not react with $NaBH_4$ under identical conditions.

Table I. The ^{1}H Resonance Average Shift ($\Delta\delta$) of the η^5-C_5H_5 and Ortho Phenyl Protons and the Resolution ($\Delta\Delta\delta$) of the η^5-C_5H_5 Resonances for **2–4**

Yb-Optishift:Fe complex molar ratio	$\Delta\Delta\delta$ (η^5-C_5H_5)[a]	$\Delta\delta$ (av η^5-C_5H_5)[a]	$\Delta\delta$ (ortho phenyl protons)[a]
(η^5-C_5H_5)Fe(CO)(CN)(PPh_3) (**4**)			
1	0.29	4.84	6.92
0.67	0.27	4.57	6.47
0.40	0.19	2.85	4.08
(η^5-C_5H_5)Fe(CO)(PPh_3)(σ-CH_2CN) (**2**)			
0.62	*b*	*b*	2.73
0.48	0.10	3.10	2.11
0.38	0.08	2.61	1.68
0.29	0.067	2.10	1.59
0.14	0.05	1.44	1.13
(η^5-C_5H_5)Fe(CO)(PPh_3)(σ-CH_2CH_2CN) (**3**)			
0.67	0	0.32	0.07
0.42	0	0.24	0.04

[a] In ppm. [b] Peak obscured by PPh_3 resonance.

Because this isocyanide compound was not reacting in a normal fashion, it was considered possible that it had rearranged to a metal nitrile compound. This could easily explain the reactions outlined above. In order to test this, a nitrile derivative was prepared by addition of acetonitrile to an equimolar mixture of **6** and $AgBF_4$ to yield in 94.5% [(η^5-C_5H_5)Fe(CO)(NCMe)(PPh_3)]BF_4 (**11**). This compound has been prepared earlier using $AlCl_3$ to assist in the removal of the halide but only in 9% yield.[10] The reactivity of **11** showed clearly that it was different from the isocyanide compound **1**. For example, it decomposes rapidly in boiling ethanol to yield [(η^5-C_5H_5)Fe(CO)$_2$(PPh_3)]BF_4.

Alkylnitrile Derivatives. In order to compare with the ^{1}H and ^{13}C nmr spectra of **4** in the presence of Yb-Optishift[1] (*vide infra*) both (η^5-C_5H_5)Fe(CO)(PPh_3)(σ-CH_2CN) (**2**) and (η^5-C_5H_5)Fe(CO)(PPh_3)(σ-CH_2CH_2CN) (**3**) were prepared. Compound **2** was synthesized in low yield by treating **6** with $LiCH_2CN$. Ferrocene and [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ were also produced. These were separated easily from the desired product by column chromatography. Compound **3** was prepared in high yield by the reaction of [(η^5-C_5H_5)Fe-(CO)(PPh_3)(η^2-C_2H_4)]BF_4 with KCN in ethanol. Both **2** and **3** are stable in the solid state and decompose very slowly in air in solution.

Nmr of 2–4, with Yb-Optishift. The ^{1}H nmr spectra of compounds **2–4** were run in $CDCl_3$ in the presence of varying concentrations of Yb-Optishift. The results of the changes in the η^5-C_5H_5 and ortho phenyl proton resonances are shown in Table I. Considerable loss in resolution was experienced with a molar ratio (Yb:Fe) in excess of 1. The average location of the η^5-C_5H_5 resonances in the cyanide complex **4** moves downfield and considerable resolution of these enantiotopic protons was observed (the magnitude of this resolution is called

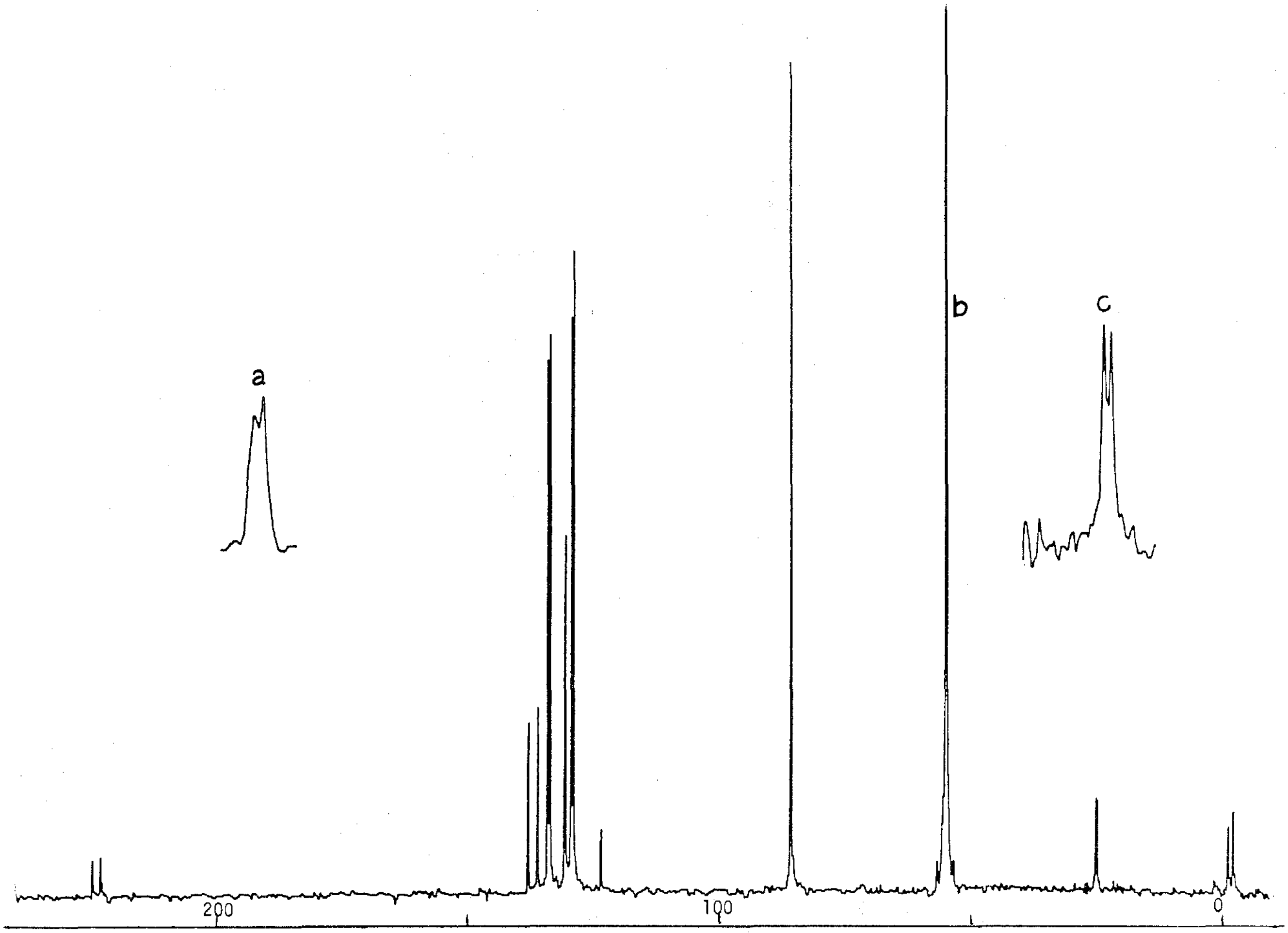

Figure 1. ^{13}C nmr spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CH_2CN)$ in ppm from TMS: (a) expansion of 123-ppm peak; (b) CH_2Cl_2 solvent; (c) expansion of 24-ppm peak. For peak assignments, see the Experimental Section.

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CH_2CN)$ (**3**) were prepared. Compound **2** was synthesized in low yield by treating **6** with $LiCH_2CN$. Ferrocene and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ were also produced. These were separated easily from the desired product by column chromatography. Compound **3** was prepared in high yield by the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}C_2H_4)]BF_4$ with KCN in ethanol. Both **2** and **3** are stable in the solid state and decompose very slowly in air in solution.

Nmr of 2–4, with Yb-Optishift. The ^{1}H nmr spectra of compounds **2**–**4** were run in $CDCl_3$ in the presence of varying concentrations of Yb-Optishift. The results of the changes in the $\eta^5\text{-}C_5H_5$ and ortho phenyl proton resonances are shown in Table I. Considerable loss in resolution was experienced with a molar ratio (Yb:Fe) in excess of 1. The average location of the $\eta^5\text{-}C_5H_5$ resonances in the cyanide complex **4** moves downfield and considerable resolution of these enantiotopic protons was observed (the magnitude of this resolution is called $\Delta\Delta\delta^9$). A similar result was found for **2** although the magnitude of the shift and $\Delta\Delta\delta$ values is lower. The methylene protons are also shifted considerably, but no doubling of the resonance could be observed. For both of these complexes, the ortho phenyl proton resonance is shifted downfield, but as with the methylene protons no resolvable doubling is observed. There is also some small shifting (less than 0.6 ppm) downfield of the resonance assigned to the meta and para protons. Very small shifts and no splitting of any resonance was observed for **3** for a molar ratio up to 0.67.

The explanation for the above trends relates to the character of the lone pair on nitrogen and thus to the strength of the complex formed in solution with the shift reagent. Whitesides, *et al.*,[9a] have recently reported that 2-cyanobutane interacts weakly with tris(3-trifluoroacetyl-*d*-nopinate)europium(III) to give a $\Delta\Delta\delta$ for the 1-methyl resonance of 0.04 ppm. Because this value of $\Delta\Delta\delta$ was considerably smaller than that observed for analogous amines and alcohols, it was concluded that nitriles weakly complex to shift reagents. A similar observation is observed in this work for **3** where the cyanide group is insulated from the metal by two methylene groups. In contrast, **4** interacts very strongly with the shift reagent yielding a maximum $\Delta\Delta\delta$ of 0.29 ppm. The strong interaction of **4** with the shift reagent was anticipated from the work of Marks, *et al.*,[8b] who have previously reported a shift of 3.81 ppm for the $\eta^5\text{-}C_5H_5$ resonance of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$ in the presence of $Eu(fod)_3$. The surprising result is that **2** behaves more like the cyanide complex, interacting strongly with the shift reagent. The metal can apparently influence the cyanide group even when insulated from it by a methylene group. A large effect of the metal on the cyanide is also indicated by the lowering of the ν(CN) for **2** to 2188 cm^{-1} compared to the normal range for nitriles of 2246–2260 cm^{-1}.

Due to the success of observing large $\Delta\Delta\delta$ values in ^{1}H nmr of these complexes, an analogous study was carried out on the ^{13}C resonances. Figure 1 shows a representative ^{13}C spectrum of complexes of the type reported in this paper. There is no observable coupling of the phosphorus to the $\eta^5\text{-}C_5H_5$ carbons (the ^{1}H–^{31}P coupling is 1.2 Hz), but there is coupling of the phosphorus to the carbons on the alkyl chain and the carbonyl carbon. Spectra run for all three compounds in the presence of a 1:1 molar ratio of Yb-Optishift show very little change. There are small shiftings (2–8 ppm) of the resonances and the only resonance that was resolved was that assigned to the ortho phenyl carbons of **4**. The $\Delta\Delta\delta$ is 0.08 ppm. The carbonyl and cyanide carbon resonances were not observed due to lower quality spectra in the presence of the Yb-Optishift. These results indicate that at least for the compounds studied here, shift reagents affect ^{1}H nmr resonances considerably more than ^{13}C nmr resonances.

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Registry No. **1**, 53897-00-0; **2**, 53897-01-1; **3**, 53897-02-2; **4**, 32757-48-5; **5**, 12100-40-2; **6**, 12099-18-2; **7**, 53897-03-3; **8**, 12078-28-3; **9**, 12152-37-3; $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}C_2H_4)]BF_4$, 41560-74-1; **11**, 53897-04-4; NaOEt, 141-52-6; KCN, 151-50-8; $NaBH_4$, 16940-66-2; Et_3OPF_6, 17950-40-2; Yb-Optishift, 38054-03-4.

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Stereochemically Nonrigid Behavior in Transition Metal Complexes. Variable-Temperature Phosphorus-31 Nuclear Magnetic Resonance Studies of Diene and Dienyl Complexes of Manganese, Rhenium, Iron, and Ruthenium Containing Phosphite Ligands

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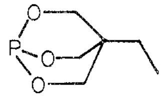
The synthesis and characterization of a complete series of complexes of the types (diene)M(CO)$_x$(EPTB)$_{3-x}$ (where diene = cyclohexadiene, cycloheptadiene; M = Fe, Ru; x = 0, 1, 2) and (dienyl)M(CO)$_x$(EPTB)$_{3-x}$ (where dienyl = cyclopentadienyl, cyclohexadienyl, cycloheptadienyl; M = Mn, Re, Fe$^+$, Ru$^+$; x = 1, 2; and EPTB = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane) is described. Low-temperature ^{31}P nmr studies of these complexes show that most of them exist as mixtures of ligand isomers and that these isomers are undergoing rapid interconversion at ambient temperatures. Computer simulation of the observed line shapes allowed the abstraction of kinetic parameters for the interconversion processes. Rates of ligand scrambling depend principally on the metal for both diene and dienyl species, decreasing in the order Mn $\sim$ Re > Fe$^+$ > Ru$^+$ for dienyl compounds and Fe > Ru for the diene complexes. Surprisingly, the formally five-coordinate diene complexes scramble only slightly faster than the formally six-coordinate dienyl complexes. The total range of rates is only a factor of about 10^4 at 220°K, suggesting that the phenomenon is probably quite general for transition metal π complexes. For the cycloheptadiene complexes, a second faster fluxional process involving equilibration of conformations of the methylene groups of the organic ligand was also observed. ^{31}P nmr chemical shifts depend principally on the central metal atom, falling in the order PMn (−50 to −30 ppm) < PFe (−30 to −5 ppm) < PRu(−7 to +17 ppm) < PRe (+15 to +35 ppm) (shifts in ppm upfield of P(OMe)$_3$). Apical and basal ligands differ by about 10 ppm, with the basal ligands at higher field. Smaller effects of ring size, charge, and degree of substitution were also observed.

Introduction

In connection with another problem, we had occasion to investigate the low-temperature ^{31}P nmr spectrum of a fairly extensive series of cyclic diene and dienyl complexes of the type (π ligand)M(CO)$_x$(EPTB)$_{3-x}$, where π ligand = η^4-cyclohexadiene or η^4-cycloheptadiene, M = Fe or Ru, and x = 1, 2, or 3 or where π ligand = η^5-cyclohexadienyl or η^5-cycloheptadienyl, M = Mn, Re, Fe$^+$, or Ru$^+$, and x = 1 or 2 and where EPTB = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, **1**. Most of these species show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interesting fluxional behavior, involving scrambling of the EPTB ligands among coordination sites at the metal, at rates which vary by a factor of about 10^4 at 220°K. In view of the