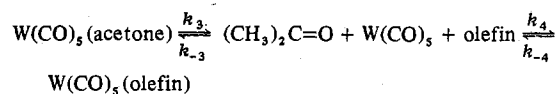


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Now the overall equilibrium constant is 21 for olefin = 1-pentene, the ratio  $k_{-3}/k_4 \approx 0.6$ , and the activation energy for acetone loss is 7 kcal/mol. These numbers imply that the activation energy for olefin loss is certainly less than 10 kcal/mol.

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## Organonitrogen Derivatives of Metal Carbonyls.

### IX. Novel Products from Reactions of Aminoalkynes with Metal Carbonyls<sup>1</sup>

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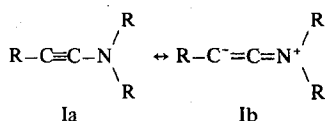
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Reaction of  $(C_2H_5)_2NC\equiv N(C_2H_5)_2$  with  $Fe(CO)_5$  or  $Fe_3(CO)_{12}$  gives a mixture of yellow  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  and the orange cyclopentadienone complex  $[(C_2H_5)_2N]_4C_4COFe(CO)_3$ . Reaction of  $C_6H_5C\equiv N(CH_3)_2$  with  $Fe(CO)_5$  in boiling octane gives orange  $C_6H_5C_2N(CH_3)_2Fe_2(CO)_6$ . Reaction of  $CH_3C\equiv N(C_2H_5)_2$  with  $Fe(CO)_5$  gives the orange cyclopentadienone complex  $[(C_2H_5)_2N]_2(CH_3)_2C_4COFe(CO)_3$ . Reaction of  $HC\equiv N(CH_3)_2$  with  $Fe_3(CO)_{12}$  gives the orange tricarbonylferrole-iron tricarbonyl complex  $[(CH_3)_2N]_2C_4H_2Fe_2(CO)_6$ . Ultraviolet irradiation of the aminoalkynes  $RC\equiv N(C_2H_5)_2$  ( $R = CH_3$  or  $N(C_2H_5)_2$ ) with  $Mn_2(CO)_{10}$  in tetrahydrofuran gives the orange complexes  $[RC_2N(C_2H_5)_2]Mn_2(CO)_8$ . Ultraviolet irradiation of  $(C_2H_5)_2NC\equiv N(C_2H_5)_2$  with  $W(CO)_6$  in tetrahydrofuran gives orange crystalline  $[(C_2H_5)_2N]_4C_4W(CO)_4$ , indicated by its proton and carbon-13 NMR spectra not to be a cyclobutadiene-tungsten tetracarbonyl derivative but instead a derivative with much lower symmetry. Reactions of  $(C_2H_5)_2NC\equiv N(C_2H_5)_2$  with  $C_5H_5M(CO)_2$  ( $M = Co$  and  $Rh$ ) give the black trimetallic derivatives  $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$  in which the carbon-carbon triple bond of the diaminoalkyne has been broken to form a trigonal-bipyramidal  $M_3C_2$  cluster with the two carbon atoms at the apices. The structures of these observed products can be rationalized by three alternative pathways for reactions of aminoalkynes with metal carbonyls: (1) oligomerization reactions involving only the carbon-carbon triple bond similar to those of other alkynes; (2) reactions of the aminoalkyne in its keteneimmonium ylide form leading to products containing  $\eta^3\text{-CCN}$  ligands with bonding of the original amino nitrogen as well as the original triple-bond carbons to the transition metal; (3) complete cleavage of the aminoalkyne carbon-carbon triple bond to give metal complexes built from aminocarbene units.

#### Introduction

Reactions of alkynes with metal carbonyls have led to numerous interesting organometallic derivatives including substituted cyclobutadiene, cyclopentadienone, metallacyclopentadiene, metallacyclohexadienone, benzene, tropone, and more complex metallocyclic derivatives as well as complexes containing monoligand monometallic, biligand bimetallic, or biligand monometallic alkyne ligands<sup>3,4</sup> including derivatives with metal-metal multiple bonds.<sup>5-7</sup> This variety of unusual and interesting products obtained from metal carbonyls and alkynes made of interest a comparable study of reactions of metal carbonyls with aminoalkynes.<sup>8</sup> The possibility for strong  $p\pi\text{-}p\pi$  bonding between the amino nitrogen and the adjacent sp carbon in aminoalkynes makes dipolar resonance structures of the type Ib significant in determining the chemistry of



aminoalkynes. The reduction of the effective bond order of the carbon-carbon triple bond by keteneimmonium ylide

resonance structures of the type Ib and the resulting increased negative charge on one of the carbon atoms should make the reactivity of aminoalkynes toward metal carbonyls considerably different from that of simple alkynes.

This paper describes a survey of some reactions of aminoalkynes with metal carbonyls. Some cyclopentadienone and metallacyclopentadiene derivatives were obtained from aminoalkynes and  $Fe(CO)_5$  or  $C_5H_5Rh(CO)_2$  in which only the carbon-carbon triple bond of the aminoalkyne interacts with the transition metal system completely analogous to well-established<sup>3,4</sup> reactions of alkynes without amino substituents. However, other reactions of aminoalkynes with iron, manganese, and tungsten carbonyls gave products in which the adjacent carbon-carbon triple bond and amino group of the aminoalkyne interact simultaneously with the metal atom to form new metal complexes of types not previously encountered in either alkyne<sup>3,4</sup> or amine<sup>9</sup> metal carbonyl derivatives. The most unusual reactions of aminoalkynes with metal carbonyls were the reactions of the diaminoalkyne  $(C_2H_5)_2NC\equiv N(C_2H_5)_2$  with  $C_5H_5M(CO)_2$  ( $M = Co$  and  $Rh$ ) to give the trimetallic derivatives  $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$  in which the carbon-carbon triple bond of the diaminoalkyne has undergone complete rupture to form a trigonal-bipyramidal cage with

carbon atoms at the apical vertices and transition metal atoms at the equatorial vertices.

### Experimental Section

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., and Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Molecular weights were determined in the indicated solvents by Schwarzkopf using vapor pressure osmometry. Infrared spectra in the  $\nu(\text{CO})$  region were taken in cyclohexane or dichloromethane and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. In addition other regions of the infrared spectra of selected compounds were investigated in potassium bromide pellets or liquid films. Each spectrum was calibrated against the  $1601\text{-cm}^{-1}$  band of polystyrene film. Proton NMR spectra were taken in  $\text{CDCl}_3$  solutions and recorded on a Varian T-60 spectrometer. Melting points were taken in capillaries and are uncorrected.

The carbon-13 NMR spectra were taken in  $\text{CDCl}_3$  solutions using a Jeolco PFT-100 spectrometer operating at 25.0336 MHz in the Fourier transform mode with proton decoupling and deuterium lock. A pulse angle of  $45^\circ$  and a pulse interval of 3 s were used. Carbon-13 chemical shifts ( $\delta$ ) are reported in ppm downfield from internal tetramethylsilane. The relative heights of some carbon-13 resonances are reported in order to provide some qualitative information regarding the magnitudes of relaxation effects, Overhauser effects, and nitrogen-14 quadrupole coupling effects of some of the more unusual carbon atoms in these complexes.

The metal carbonyl derivatives  $\text{Mn}_2(\text{CO})_{10}$ ,<sup>10</sup>  $\text{Fe}_3(\text{CO})_{12}$ ,<sup>11</sup> and  $\text{C}_5\text{H}_5\text{M}(\text{CO})_2$  ( $\text{M} = \text{Co}^{12}$  and  $\text{Rh}^{13,14}$ ) were prepared by the cited published procedures. The transition metal derivatives  $\text{W}(\text{CO})_6$  (Pressure Chemical Co., Pittsburgh, Pa.),  $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$  (Ethyl Corp., New York, N.Y.),  $\text{Fe}(\text{CO})_5$  (GAF Corp., New York, N.Y.),  $\text{Co}_2(\text{CO})_8$  (Strem Corp., Danvers, Mass.), and  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (Englehard Corp., Newark, N.J.) were purchased from the indicated commercial suppliers. The aminoalkynes were prepared by standard methods.<sup>8,15</sup>

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling filtered solutions of organometallic compounds, (c) filling evacuated vessels containing organometallic compounds. Alcoa F-20 alumina from Bauxite, Ark., or commercial Florisil was used for chromatography as indicated. Ultraviolet irradiations were performed with an Englehard-Hanovia medium-pressure mercury lamp immersed in a water-cooled Pyrex well in the reaction vessel. Tetrahydrofuran was purified by distillation over sodium benzophenone ketyl under nitrogen immediately before use.

**Reaction of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  with  $\text{Fe}(\text{CO})_5$ .** A mixture of 5.0 g (30 mmol) of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$ , 10 g (51 mmol) of  $\text{Fe}(\text{CO})_5$ , and 100 ml of *n*-octane was boiled under reflux for 18 h. Solvent was then removed at  $40\text{--}60^\circ\text{C}$  (20 mm). The residue was extracted with  $\sim 150$  ml of dichloromethane. The dichloromethane extracts were filtered from a black insoluble pyrophoric residue. The filtrate was concentrated to  $\sim 10$  ml and then chromatographed on a  $2 \times 100$  cm alumina column. After development of the chromatogram with hexane a yellow band of  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{C}_2\text{Fe}_2(\text{CO})_6$  was eluted with hexane. After removal of this product, the orange band of  $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{C}_4\text{COFe}(\text{CO})_3$  was eluted with a 1:1 mixture of dichloromethane and hexane. The products were isolated by evaporation of the eluates followed by recrystallization from pentane. The yields of  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{C}_2\text{Fe}_2(\text{CO})_6$  and  $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{C}_4\text{COFe}(\text{CO})_3$  were 1.85 g (16%) and 4.7 g (63%), respectively.

Properties of  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{C}_2\text{Fe}_2(\text{CO})_6$ : yellow crystals, mp  $103\text{--}105^\circ\text{C}$ , sublimes  $100^\circ\text{C}$  (0.01 mm).

Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{Fe}_2\text{N}_2\text{O}_6$ : C, 43.0; H, 4.5; N, 6.3; O, 21.5; mol wt 448. Found: C, 43.4; H, 4.7; N, 6.2; O, 21.6; mol wt 471 (acetone).

Infrared spectrum:  $\nu(\text{CH})$  frequencies at 3000 (vw), 2980 (w), 2937 (w), and 2870 (vw)  $\text{cm}^{-1}$ ;  $\nu(\text{CO})$  frequencies at 2054 (s), 2009 (s), 1997 (s), 1976 (s), 1937 (s), and 1929 (s)  $\text{cm}^{-1}$ ; other bands at 1540 (s), 1460 (m), 1443 (m), 1383 (m), 1347 (m), 1270 (m), 1178 (m), 1155 (m), 1092 (vw), 1074 (w), 1045 (w), 994 (vw), 937 (w), 832 (m), 795 (w), 767 (m), and 739 (m)  $\text{cm}^{-1}$ .

Proton NMR spectrum: resonances at  $\tau$  6.13 (quartet,  $J = 7$  Hz) and 8.71 (triplet,  $J = 7$  Hz) of approximate relative intensities 2:3 corresponding to the  $\text{CH}_2$  and  $\text{CH}_3$  protons, respectively.

Carbon-13 NMR spectrum: resonances at  $\delta$  257.6 (height 2.0), 214.8 (height 4.5), 57.5 (height 11.7), and 13.7 (height 6.7) corresponding to the original alkyne carbons, the metal carbonyl carbons, the  $\text{CH}_2$  carbons, and the  $\text{CH}_3$  carbons, respectively.

Properties of  $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{C}_4\text{COFe}(\text{CO})_3$ : orange crystals, mp  $119\text{--}121^\circ\text{C}$ , sublimes at  $100^\circ\text{C}$  (0.01 mm).

Anal. Calcd for  $\text{C}_{24}\text{H}_{40}\text{FeN}_4\text{O}_4$ : C, 57.2; H, 8.0; N, 11.1; O, 12.7; mol wt 504. Found: C, 57.3; H, 8.1; N, 10.9; O, 12.5; mol wt 499 (benzene).

Infrared spectrum:  $\nu(\text{CH})$  frequencies at 2970 (m), 2930 (m), 2870 (w), and 2820 (vw)  $\text{cm}^{-1}$ ; metal  $\nu(\text{CO})$  frequencies at 2045 (s) and 1962 (s)  $\text{cm}^{-1}$ ; ketonic  $\nu(\text{CO})$  frequency at 1602 (s)  $\text{cm}^{-1}$ ; other bands at 1482 (m), 1449 (m), 1375 (m), 1330 (vw), 1320 (vw), 1294 (w), 1279 (w), 1270 (vw), 1224 (m), 1206 (w), 1177 (w), 1130 (w), 1110 (w), 1078 (w), 1049 (m), 937 (w), 823 (w), 795 (w), and 742 (m)  $\text{cm}^{-1}$ .

Proton NMR spectrum: resonances at  $\tau$  6.66 (apparent quintet,  $J = 7$  Hz) and 8.81 (triplet,  $J = 7$  Hz) of approximate relative intensities 2:3 corresponding to the  $\text{CH}_2$  and  $\text{CH}_3$  protons, respectively.

Carbon-13 NMR spectrum: resonances at  $\delta$  211.0 (height 2.6), 159.8 (height 1.0), 108.4 (height 2.0), 95.9 (height 1.8), 44.7 (height 3.8), 42.9 (height 3.7), 13.0 (height 3.0), and 12.4 (height 2.8) corresponding to the metal carbonyl carbons, the cyclopentadienone carbonyl carbon, the two other types of cyclopentadienone ring carbons, two types of ethyl  $\text{CH}_2$  carbons, and two types of ethyl  $\text{CH}_3$  carbons, respectively.

**Reaction of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  with  $\text{Fe}_3(\text{CO})_{12}$ .** A mixture of 1.6 g (9.5 mmol) of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$ , 7.0 g (13.9 mmol) of  $\text{Fe}_3(\text{CO})_{12}$ , and 100 ml of hexane was boiled under reflux for 30 h. Chromatography of the reaction mixture by a procedure similar to that described above gave 0.81 g (19% yield) of  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{C}_2\text{Fe}_2(\text{CO})_6$  and 0.23 g (10% yield) of  $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{C}_4\text{COFe}(\text{CO})_3$  identified by their infrared spectra and melting points.

**Ultraviolet Irradiation of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  with  $\text{Fe}(\text{CO})_5$ .** A mixture of 2.0 g (11.9 mmol) of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$ , 10 g (51 mmol) of  $\text{Fe}(\text{CO})_5$ , and 250 ml of hexane was exposed to ultraviolet irradiation for 20 h. Chromatography of the reaction mixture by a procedure similar to that described above gave 0.37 g (7% yield) of  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{C}_2\text{Fe}_2(\text{CO})_6$  and 1.2 g (40% yield) of  $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{C}_4\text{COFe}(\text{CO})_3$ .

**Reaction of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  with  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{C}_2\text{Fe}_2(\text{CO})_6$ .** A mixture of 0.8 g (4.8 mmol) of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$ , 0.45 g (1.0 mmol) of  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{C}_2\text{Fe}_2(\text{CO})_6$ , and 100 ml of redistilled tetrahydrofuran was boiled under reflux in a carbon monoxide atmosphere for 15 h. Removal of solvent at  $\sim 25^\circ\text{C}$  (35 mm) followed by chromatography on a  $2 \times 80$  cm Florisil column gave an orange band, which was eluted with pentane. Evaporation of the eluate gave 0.13 g (17% yield based on CO) of orange  $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{C}_4\text{COFe}(\text{CO})_3$ , mp  $117\text{--}119^\circ\text{C}$ , identified by its infrared spectrum.

**Reaction of  $\text{C}_6\text{H}_5\text{C}\equiv\text{CN}(\text{CH}_3)_2$  with  $\text{Fe}(\text{CO})_5$ .** A mixture of 1.5 g (10.3 mmol) of  $\text{C}_6\text{H}_5\text{C}\equiv\text{CN}(\text{CH}_3)_2$ , 3.0 g (15.3 mmol) of  $\text{Fe}(\text{CO})_5$ , and 50 ml of octane was boiled under reflux for 16 h. Removal of solvent, extraction with dichloromethane, and chromatography on alumina by a procedure similar to that described above for the reaction of  $(\text{C}_2\text{H}_5)_2\text{NC}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  with  $\text{Fe}(\text{CO})_5$  gave a yellow band, which was eluted with hexane. Evaporation of this eluate at  $\sim 25^\circ\text{C}$  (25 mm) gave an oil which crystallized upon slow evaporation from hexane to give 2.1 g (69% yield) of orange  $\text{C}_6\text{H}_5\text{C}_2\text{N}(\text{CH}_3)_2\text{Fe}_2(\text{CO})_6$ , dec pt  $127^\circ\text{C}$ .

Anal. Calcd for  $\text{C}_{16}\text{H}_{11}\text{Fe}_2\text{NO}_6$ : C, 45.2; H, 2.6; N, 3.3; O, 22.6; mol wt 425. Found: C, 44.9; H, 2.5; N, 3.4; O, 23.1; mol wt 353 (acetonitrile).

Infrared spectrum:  $\nu(\text{CO})$  frequencies (cyclohexane) at 2091 (m), 2023 (s), 1998 (s), 1986 (s), 1966 (m), and 1950 (s)  $\text{cm}^{-1}$ .

Proton NMR spectrum: resonances at  $\tau$  2.91 (singlet), 6.60 (singlet), and 6.98 (singlet) of approximate relative intensities 5:3:3 corresponding to the five phenyl protons and three protons each of two nonequivalent methyl groups.

Carbon-13 NMR spectrum: resonances at  $\delta$  228.3 (height 1.0), 211 (broad hump, height  $\sim 0.3$ ), 146.3 (height 1.0), 129.1 (height 8.0), 128.3 (height 7.6), 126.3 (height 3.9), 102.6 (height 0.6), and 44.7 (height 2.3).

**Reaction of  $\text{CH}_3\text{C}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  with  $\text{Fe}(\text{CO})_5$ .** A mixture of 1.2 g (10.8 mmol) of  $\text{CH}_3\text{C}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$ , 5.0 g (25.5 mmol) of  $\text{Fe}(\text{CO})_5$ , and 100 ml of *n*-octane was boiled under reflux for 20 h. Removal of solvent, extraction with dichloromethane, and chromatography on

alumina by a procedure similar to that described above for the reaction of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with  $Fe(CO)_5$  gave an orange band, which was eluted with hexane. Evaporation of this eluate at 25 °C (35 mm) gave a red oil. Evaporative distillation<sup>1</sup> of this oil at 90 °C (0.01 mm) for 2 days gave 0.86 g (41% yield) of a red liquid which solidified on standing to give orange crystalline  $[(C_2H_5)_2N]_2(C_4H_3)_2C_4COFe(CO)_3$ , mp 37–39°.

Anal. Calcd for  $C_{18}H_{26}FeN_2O_4$ : C, 56.3; H, 7.2; N, 7.7. Found: C, 56.1; H, 7.0; N, 7.2.

Infrared spectrum: metal  $\nu(CO)$  frequencies (cyclohexane) at 2041 (vs), 1977 (vs), and 1956 (vs)  $cm^{-1}$ ; ketonic  $\nu(CO)$  frequency at 1641 (s)  $cm^{-1}$ .

Proton NMR spectrum: overlapping quartet ( $J = 7$  Hz) ethyl  $CH_2$  resonances at  $\tau$  6.69, 6.75, and 6.82 of approximate relative intensities 1:1:2, respectively; singlet  $CH_3$  resonances at  $\tau$  7.81 and 8.11 of approximate relative intensities 1:1; triplet ( $J = 7$  Hz) ethyl  $CH_3$  resonances at  $\tau$  8.88 and 8.90 of approximate relative intensities 3:1, respectively.

Carbon-13 NMR spectrum: resonances at  $\delta$  210.3 (height 2.3), 161.8 (height 1.0), 124.3 (height 1.1), 110.2 (height 1.0), 80.5 (height 1.3), 74.5 (height 1.0), 45.5 (height 3.1), 13.0 (height 3.8), and 10.5 (height 0.8) corresponding to the metal carbonyl carbons, the cyclopentadienone carbonyl carbon, the four other types of cyclopentadienone ring carbons, the ethyl  $CH_2$  carbons, and two types of  $CH_3$  carbons, respectively.

**Reaction of  $HC\equiv CN(CH_3)_2$  with  $Fe_3(CO)_{12}$ .** A solution of 5.0 g (9.9 mmol) of  $Fe_3(CO)_{12}$  in 150 ml of hexane was treated with 1.0 g (14.5 mmol) of  $HC\equiv CN(CH_3)_2$ . The originally green reaction mixture soon became orange. After 15 h of boiling under reflux, solvent was removed from the reaction mixture at  $\sim 25$  °C (35 mm). The residue was chromatographed on a  $2 \times 80$  cm Florisil column in pentane solution. The first yellow band was eluted with pentane. Evaporation of the eluate followed by low-temperature crystallization from pentane gave 0.24 g (8% yield) of orange  $[(CH_3)_2N]_2C_4H_2Fe_2(CO)_6$ , mp 61–64 °C.

A red-orange band followed the yellow band of  $[(CH_3)_2N]_2C_4H_2Fe_2(CO)_6$ . Elution of this red band with dichloromethane followed by evaporation of the eluate gave an oil, shown by its infrared spectrum to contain a negligible amount of metal carbonyl derivatives. This product was not investigated further.

Anal. Calcd for  $C_{14}H_{14}Fe_2N_2O_6$ : C, 40.2; H, 3.3; N, 6.7; mol wt 438. Found: C, 40.2; H, 3.4; N, 6.6; mol wt 424 (benzene).

Infrared spectrum:  $\nu(CH)$  frequencies at 3018 (vw), 2988 (vw), 2953 (w), 2860 (vw), 2833 (vww), and 2784 (vw)  $cm^{-1}$ ;  $\nu(CO)$  frequencies (cyclohexane) at 2072 (m), 2027 (s), 1978 (s), 1972 (s), and 1939 (w)  $cm^{-1}$ ; other bands at 1492 (m), 1478 (m), 1453 (w, sh), 1440 (m), 1403 (m), 1381 (m), 1332 (w), 1295 (w), 1256 (vw), 1223 (w), 1189 (w), 1160 (w), 1127 (m), 1093 (vw), 1069 (m), 1052 (w), 941 (w), 908 (w), 890 (w), 871 (w), 792 (vw), 709 (vw), 690 (m), and 665 (m)  $cm^{-1}$ .

Proton NMR spectrum: singlet resonances at  $\tau$  4.11 and 7.23 of approximate relative intensities 1:6, respectively, corresponding to the single ferrole ring proton and the  $(CH_3)_2N$  protons, respectively.

Carbon-13 NMR spectrum: resonances at  $\delta$  212.0 (height 2.2), 147.7 (height 2.0), 123.0 (height 4.5), and 40.8 (height 5.7) corresponding to the carbonyl carbons, the ferrole ring carbons bonded to  $N(CH_3)_2$  groups, the ferrole ring carbons bonded to H atoms, and the  $N(CH_3)_2$  carbons, respectively.

**Reaction of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with  $Mn_2(CO)_{10}$ .** A mixture of 1.6 g (9.5 mmol) of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ , 2.0 g (5.1 mmol) of  $Mn_2(CO)_{10}$ , and 250 ml of tetrahydrofuran was exposed to ultraviolet irradiation for 16 h. Solvent was removed from the filtered reaction mixture at 25 °C (35 mm). The residue was chromatographed on a  $2 \times 100$  cm Florisil column. The orange band was eluted with 1:1 mixture of dichloromethane and hexane. Evaporation of the eluate at  $\sim 25$  °C (25 mm) followed by crystallization from a 1:1 mixture of dichloromethane and hexane gave 0.21 g (8.2% yield) of orange  $(C_2H_5)_2NC_2N(C_2H_5)_2Mn_2(CO)_8$ , mp 83–86 °C.

Anal. Calcd for  $C_{18}H_{20}Mn_2N_2O_8$ : C, 43.0; H, 4.0; N, 5.6; O, 25.5; mol wt 502. Found: C, 43.1; H, 4.3; N, 5.4; O, 25.4; mol wt 500 (benzene).

Infrared spectrum:  $\nu(CO)$  frequencies at 2062 (m), 1992 (s), 1965 (s), 1948 (s), 1932 (s), and 1917 (s)  $cm^{-1}$ .

Carbon-13 NMR spectrum: resonances at  $\delta$  49.4 (height 5.9), 49.1 (height 6.0), 12.5 (height 3.5), and 11.9 (height 3.9) corresponding to two types of ethyl  $CH_2$  carbons and two types of ethyl  $CH_3$  carbons,

respectively. The remaining carbons were not detected apparently because of excessive quadrupole broadening by the manganese atoms to which they are bonded.

**Reaction of  $CH_3C\equiv CN(C_2H_5)_2$  with  $Mn_2(CO)_{10}$ .** A mixture of 2.0 g (18.0 mmol) of  $CH_3C\equiv CN(C_2H_5)_2$ , 3.0 g (7.7 mmol) of  $Mn_2(CO)_{10}$ , and 250 ml of tetrahydrofuran was exposed to ultraviolet irradiation for 20 h. Removal of solvent and chromatography on Florisil similar to the procedure described above for the reaction between  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and  $Mn_2(CO)_{10}$  gave a red-orange band which was eluted with a mixture of hexane and dichloromethane. Evaporation of this eluate gave a red oil which crystallized upon treatment with pentane. Recrystallization of the solid from a mixture of dichloromethane and heptane gave 0.57 g (17% yield) of orange  $CH_3C_2N(C_2H_5)_2Mn_2(CO)_8$ , mp 85 °C dec.

Anal. Calcd for  $C_{15}H_{13}Mn_2NO_8$ : C, 40.5; H, 2.9; N, 3.1; O, 28.8; mol wt 445. Found: C, 40.7; H, 2.9; N, 3.3; O, 28.6; mol wt 405 (benzene).

Infrared spectrum:  $\nu(CO)$  frequencies (cyclohexane) at 2080 (w), 2027 (m), 1980 (s), 1966 (m), 1957 (m), 1944 (w), and 1935 (m)  $cm^{-1}$ .

Proton NMR spectrum: overlapping ethyl  $CH_2$  quartets ( $J = 7$  Hz) at  $\tau$  6.35 and 6.58;  $CH_3$  singlet at  $\tau$  7.23; overlapping ethyl  $CH_3$  triplets ( $J = 7$  Hz) at  $\tau$  8.66 and 8.75.

Carbon-13 NMR spectrum: resonances at  $\delta$  232.9 (height 1.0), 221.0 (very broad and complex, height 0.9), 136.8 (height 1.6), 54.0 (height 6.3), 50.6 (height 5.8), 30.2 (height 4.8), 14.0 (height 3.9), and 13.2 (height 4.1).

**Other Reactions of Dimetal Decacarbonyls with Aminoalkynes. (a)  $Mn_2(CO)_{10}$  and  $C_6H_5C\equiv CN(CH_3)_2$ .** A mixture of 2.0 g (5.1 mmol) of  $Mn_2(CO)_{10}$ , 2.0 g (13.8 mmol) of  $C_6H_5C\equiv CN(CH_3)_2$ , and 250 ml of tetrahydrofuran was exposed to ultraviolet irradiation for 20 h. Removal of solvent followed by chromatography on Florisil gave an orange band. Elution of this band with 1:3 hexane–dichloromethane followed by evaporation of the eluate gave an orange oil which could not be crystallized and which was too thermally unstable to purify by evaporative vacuum distillation. The infrared spectrum of this oil exhibited  $\nu(CO)$  frequencies at 2140 (m), 2070 (s), 2000 (vs), 1960 (sh), and 1915 (m)  $cm^{-1}$  consistent with  $C_6H_5C_2N(CH_3)_2Mn_2(CO)_8$  as a major component of this oil.

**(b)  $Re_2(CO)_{10}$  and  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ .** A mixture of 0.5 g (0.77 mmol) of  $Re_2(CO)_{10}$ , 1.5 g (8.9 mmol) of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ , and 250 ml of tetrahydrofuran was exposed to ultraviolet irradiation for 20 h. The infrared spectrum indicated that only decomposition had taken place with the formation of no new rhenium carbonyl derivatives.

**Reaction of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with  $W(CO)_6$ .** A mixture of 1.7 g (10 mmol) of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ , 0.7 g (2 mmol) of  $W(CO)_6$ , and 250 ml of tetrahydrofuran was exposed to ultraviolet irradiation for 24 h. Removal of solvent followed by chromatography on a  $2 \times 100$  cm alumina column gave an orange band, which was eluted with 1:10 dichloromethane–hexane to give 0.77 g (61% yield) of orange crystalline  $[(C_2H_5)_2N]_4C_4W(CO)_4$ , mp  $\sim 130$  °C dec. The product could be recrystallized by Soxhlet extraction with pentane or from a mixture of dichloromethane and hexane.

Anal. Calcd for  $C_{24}H_{40}N_4O_4W$ : C, 45.6; H, 6.3; N, 8.9; O, 10.1; mol wt 632. Found: C, 45.3; H, 6.4; N, 8.2; O, 10.5; mol wt 687 (benzene).

Infrared spectrum:  $\nu(CH)$  frequencies at 2966 (s), 2930 (m), and 2868 (w)  $cm^{-1}$ ;  $\nu(CO)$  frequencies at 1993 (s), 1890 (s), 1878 (vs), and 1850 (s)  $cm^{-1}$ ;  $\nu(C=N)$  frequency at 1572 (s)  $cm^{-1}$ ; other bands at 1505 (w), 1442 (m), 1383 (m), 1340 (w), 1284 (w), 1236 (w), 1196 (w), 1180 (w), 1168 (w), 1068 (m), 990 (w), 890 (w), 814 (w, br), 768 (w), and 737 (w)  $cm^{-1}$ .

Proton NMR spectrum: multiple overlapping ethyl  $CH_2$  quartets in the range  $\tau$  5.7–7.6 with the most prominent ones centered at  $\tau$  6.69 and 7.39; multiple overlapping ethyl  $CH_3$  triplets in the range  $\tau$  8.6–9.1 with the most prominent ones centered at  $\tau$  8.70 and 8.97.

Carbon-13 NMR spectrum: resonances at  $\delta$  245.2 (height 12.3), 244.9 (height 6.4), 220.5 (height 7.0), 218.6 (height 8.3), 210.1 (height 8.3), 207.6 (height 9.9), 144.7 (height 7.6), 143.7 (height 24.0), 123.3 (height 13.2), 70.7 (height 36.8), 67.2 (height 12.3), 62.7 (height 14.7), 61.9 (height 34.1), 60.0 (height 35.0), 55.8 (height 30.1), 49.7 (height 29.0), 49.0 (height 27.1), 44.8 (height 19.5), 43.2 (height 51.1), 42.3 (height 11.4), 38.6 (height 24.7), 18.9 (height 8.0), 18.0 (height 18.9), 15.8 (height 21.7), 15.1 (height 28.4), 14.6 (height 53.4), 13.9 (height 25.9), and 12.7 (height 43.5).

**Other Reactions of Aminoalkynes with Metal Hexacarbonyls.** The following reactions failed to give any new metal carbonyl compounds after attempted chromatography of the reaction mixtures on Florisil similar to the procedures used above: (a) ultraviolet irradiation of 1.6 g of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with 3.0 g of  $Cr(CO)_6$  in 250 ml of tetrahydrofuran for 2 h; (b) reaction of 1.6 g of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with 3.0 g of  $Mo(CO)_6$  in 100 ml of boiling 2,2,5-trimethylhexane for 20 h; (c) ultraviolet irradiation of 0.6 g of  $CH_3C\equiv CN(C_2H_5)_2$  with 5 g of  $Mo(CO)_6$  in 250 ml of tetrahydrofuran.

**Reaction of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with  $C_5H_5Co(CO)_2$ .** A mixture of 1.0 g (5.9 mmol) of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ , 1.0 g (5.6 mmol) of  $C_5H_5Co(CO)_2$ , and 75 ml of 2,2,5-trimethylhexane was boiled under reflux for 20 h. Removal of solvent at  $\sim 25^\circ C$  (0.1 mm) followed by chromatography on a Florisil column gave a deep red band, which was eluted with hexane. Evaporation of the hexane eluate at  $\sim 25^\circ C$  (35 mm) followed by slow recrystallization from hexane gave 0.34 g (33% yield) of large black crystals of  $(C_5H_5)_3Co_3C_2[N(C_2H_5)_2]_2$ , mp 165–167  $^\circ C$ .

Anal. Calcd for  $C_{25}H_{35}Co_3N_2$ : C, 55.6; H, 6.5; N, 5.2; mol wt 540. Found: C, 56.2; H, 6.7; N, 5.1; mol wt 490 (benzene).

Infrared spectrum:  $\nu(CH)$  frequencies at 3080 (vw, br), 2960–2910 (vw, vbr), and 2840 (vww)  $cm^{-1}$ ; other bands at 1446 (w), 1379 (m), 1338 (m), 1237 (m), 1179 (w), 1111 (m), 1002 (w), 835 (w), 788 (m), and 717 (w)  $cm^{-1}$ .

Proton NMR spectrum: resonances at  $\tau$  5.41 (broad), 5.70 (singlet), and 8.53 (broad) of approximate relative intensities 8:15:12, respectively, corresponding to the  $CH_2$ ,  $C_5H_5$ , and  $CH_3$  protons, respectively.

Carbon-13 NMR spectrum ( $C_6D_6$ ): resonances at  $\delta \sim 321$  (broad, height 0.13), 82.5 (height 15.0), 53.2 (height 4.8), and 14.7 (height 2.5) corresponding to the original alkyne carbons, the cyclopentadienyl carbons, the ethyl  $CH_2$  carbons, and the ethyl  $CH_3$  carbons, respectively.

**Reaction of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with  $C_5H_5Rh(CO)_2$ .** A mixture of 2.0 g (12 mmol) of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ , 2.0 g (9 mmol) of  $C_5H_5Rh(CO)_2$ , and 75 ml of octane was boiled under reflux for 20 h. Octane was then removed at  $\sim 25^\circ C$  (1 mm) and the residue chromatographed on a  $2 \times 50$  cm Florisil column. Elution of the first major band (red-brown) with hexane followed by evaporation of the eluate and recrystallization from pentane gave 0.52 g (26% yield) of black  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$ . Elution of the second major band (yellow-brown) with dichloromethane followed by evaporation of the eluate and two low-temperature crystallizations from pentane gave 0.61 g (19% yield) of orange  $[(C_2H_5)_2N]_4C_4CORhC_5H_5$ .

A similar reaction of 0.85 g (5 mmol) of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and 3.25 g (14.5 mmol) of  $C_5H_5Rh(CO)_2$  in 75 ml of boiling octane for 20 h gave 2.1 g (65% yield) of  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$  but no  $[(C_2H_5)_2N]_4C_4CORhC_5H_5$  after chromatography on Florisil by a procedure similar to that described above.

Properties of  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$ : black needles, mp 150–153  $^\circ C$ .

Anal. Calcd for  $C_{25}H_{35}N_2Rh_3$ : C, 44.7; H, 5.2; N, 4.2; mol wt 672. Found: C, 44.7; H, 5.3; N, 4.2; mol wt 652 (benzene).

Infrared spectrum:  $\nu(CH)$  frequencies at 3094 (vw), 2963 (w), 2918 (vw), and 2850 (vw)  $cm^{-1}$ ; other bands at 1446 (w), 1388 (m), 1286 (vw), 1242 (s), 1186 (m), 1115 (m), 1105 (m), 1051 (vw), 997 (w), 830 (w), 773 (s), and 734 (m)  $cm^{-1}$ .

Proton NMR spectrum: resonances at  $\tau$  4.97 (singlet), 6.39 (quartet,  $J = 7$  Hz), and 8.84 (triplet,  $J = 7$  Hz) of approximate relative intensities 15:8:12, respectively, corresponding to the  $C_5H_5$ ,  $CH_2$ , and  $CH_3$  protons, respectively.

Carbon-13 NMR spectrum: resonances at  $\delta$  280.6 (1:3:3:1 quartet,  $J = 40$  Hz, height of center peaks 0.56), 84.6 (height 15.0), 51.6 (height 6.3), and 13.4 (height 3.8) corresponding to the original alkyne carbons, the cyclopentadienyl carbons, the ethyl  $CH_2$  carbons, and the ethyl  $CH_3$  carbons, respectively.

Properties of  $[(C_2H_5)_2N]_4C_4CORhC_5H_5$ : orange crystals, mp 88–90  $^\circ C$ .

Anal. Calcd for  $C_{26}H_{45}N_4ORh$ : C, 58.6; H, 8.5; N, 10.5; mol wt 529. Found: C, 58.5; H, 8.5; N, 10.5; mol wt 453 (1,2-dichloroethane).

Infrared spectrum:  $\nu(CH)$  frequencies at 3180 (w), 2961 (s), 2920 (s), and 2861 (s)  $cm^{-1}$ ;  $\nu(CO)$  frequency at 1583 (s)  $cm^{-1}$ ; other bands at 1478 (s), 1440 (s), 1370 (s), 1334 (w), 1291 (m), 1275 (w), 1218 (m), 1210 (m), 1172 (m), 1129 (w), 1100 (m), 1032 (s), 1010 (w),

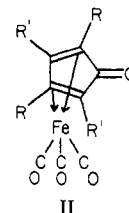
997 (w), 960 (w), 930 (w), 912 (w), 828 (w), 795 (s), 789 (s), and 732 (m)  $cm^{-1}$ .

Proton NMR spectrum: resonances at  $\tau$  5.05 (singlet), 7.14 (quartet,  $J = 7$  Hz), 9.23 (triplet,  $J = 7$  Hz), and 9.28 (triplet,  $J = 7$  Hz) of approximate relative intensities 5:16:12:12, respectively, corresponding to the  $C_5H_5$ , ethyl  $CH_2$ , and two types of ethyl  $CH_3$  protons, respectively.

Carbon-13 NMR spectrum: resonances at  $\delta$  149.6 (singlet, height 0.7), 100.9 (doublet,  $J(Rh-C) = 10$  Hz, height 2.0), 97.4 (doublet,  $J(Rh-C) = 9$  Hz, height 1.9), 84.5 (doublet,  $J(Rh-C) = 6$  Hz, height 17.8), 45.0 (singlet, height 25.4), 44.4 (singlet, height 22.6), 13.3 (singlet, height 17.9), and 12.9 (singlet, height 16.8) corresponding to the cyclopentadienone carbonyl carbon, the two other types of cyclopentadienone ring carbons, the five equivalent cyclopentadienyl carbons, the two types of ethyl  $CH_2$  carbons, and the two types of ethyl  $CH_3$  carbons, respectively.

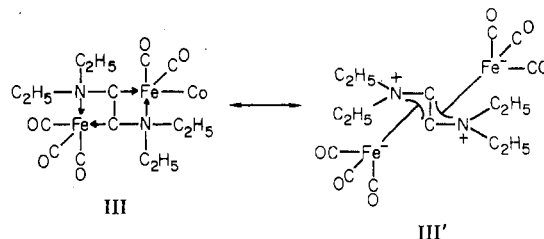
## Results

The reaction between the diaminoalkyne  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and iron carbonyls under various conditions gave two new iron carbonyl derivatives. One of these products was the orange crystalline cyclopentadienone-iron tricarbonyl derivative  $[(C_2H_5)_2N]_4C_4COFe(CO)_3$  (II;  $R = R' =$



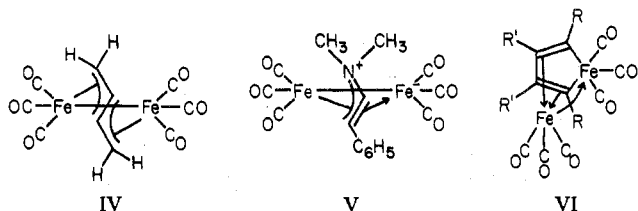
$(C_2H_5)_2N$ ) similar to numerous cyclopentadienone-iron tricarbonyl derivatives obtained from other alkynes and iron carbonyls.<sup>3,4</sup> The proton and carbon-13 NMR spectra of  $[(C_2H_5)_2N]_4C_4COFe(CO)_3$  both indicate two different types of ethyl groups in a 1:1 ratio in accord with structure II ( $R = R' = N(C_2H_5)_2$ ).

The second product from reactions of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with iron carbonyls is a yellow solid of stoichiometry  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  which does not correspond to any of the derivatives normally obtained from iron carbonyls and alkynes without amino substituents,<sup>3,4</sup> leading to an immediate suspicion that both the carbon-carbon triple bond and at least one amino nitrogen are involved in the metal-ligand bonding. The equivalence of the four ethyl groups in  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  is indicated by both the proton and carbon-13 NMR spectra. The carbon-13 resonance from the alkyne carbons has shifted far downfield to  $\delta$  257.6 in  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  similar to the positions of the carbene carbon resonances in aminocarbene-metal pentacarbonyl derivatives. All of these spectroscopic data on  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  suggest formulation of this complex as III in which the diaminoalkyne functions as a bisbidentate (i.e. tetraligate bimetallic) ligand with each bidentate portion bonded to an iron atom through both a nitrogen lone pair and an aminocarbene lone pair.<sup>26</sup> Each iron atom in III has the favored rare gas electronic configuration without forming any iron-iron bonds. A resonance hybrid of III (III') with the diaminoalkyne



functioning as a bis( $\eta^3$ -CCN) ligand similar to the bis( $\eta^3$ -

butatriene ligand in  $C_4H_4Fe_2(CO)_6$  (IV)<sup>16</sup> is possible.



However, a rather different type of alternative structure for this yellow complex  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  with an iron-iron double bond and no bonding of the amino nitrogens to the iron atom analogous to the reported structure<sup>7</sup> for the deep green  $[(CH_3)_3C]_2C_2Fe_2(CO)_6$  appears unlikely on the basis of the striking color difference between the two compounds.

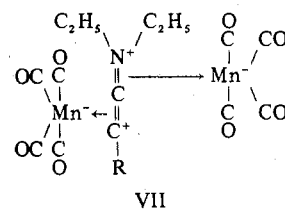
The reaction between the aminoalkyne  $C_6H_5C\equiv CN(CH_3)_2$  and  $Fe(CO)_5$  gave an orange product of stoichiometry  $C_6H_5C_2N(CH_3)_2Fe_2(CO)_6$ , which again does not correspond to that of any known products from simple alkynes and iron carbonyls.<sup>3,4</sup> This complex appears to have structure V containing a  $\eta^3$ -CCN ligand-iron bond similar to the two ligand-iron bonds in III' and giving both iron atoms the favored rare gas electronic configuration after forming an iron-iron single bond. However, the spectroscopic data do not provide definitive structural information because of the low symmetry of the complex. In the carbon-13 NMR spectrum of  $C_6H_5C_2N(CH_3)_2Fe_2(CO)_6$  the broad resonance at  $\delta$  211 can be assigned to the six carbonyl carbons, the resonances at  $\delta$  146.3, 129.1, 128.3, and 126.3 can be assigned to the four different types of phenyl carbons, the resonance at  $\delta$  44.7 can be assigned to the two methyl carbons, and the resonances at  $\delta$  228.3 and 102.6 can be assigned to the remaining two carbons which arise from the sp triple-bond carbons of the alkyne.

The remaining products obtained from aminoalkynes and iron carbonyls correspond to well-established types of products obtained from simple alkynes and iron carbonyls.<sup>3,4</sup> The aminoalkyne  $CH_3C\equiv CN(C_2H_5)_2$  reacts with  $Fe(CO)_5$  to give the cyclopentadienone derivative  $[(C_2H_5)_2N]_2(C_2H_5)_2C_4C-OFe(CO)_3$  suggested to be the unsymmetrical derivative II ( $R = N(C_2H_5)_2$ ,  $R' = CH_3$ ) by the observation of five distinct carbon-13 NMR resonances for the five cyclopentadienone ring carbons. The aminoalkyne  $HC\equiv CN(CH_3)_2$  reacts with  $Fe_3(CO)_{12}$  to give the tricarbonylferrole-iron tricarbonyl derivative  $[(CH_3)_2N]_2C_4H_2Fe_2(CO)_6$  indicated to be a symmetrical isomer VI ( $R = H$ ,  $R' = N(CH_3)_2$ ;  $R = N(CH_3)_2$ ,  $R' = H$ ) by the observations of single ring proton and single methyl proton resonances in the proton NMR spectrum and of only two ring carbon resonances and a single methyl carbon resonance in the carbon-13 NMR spectrum. A reliable decision between the two possible symmetrical isomers of  $[(CH_3)_2N]_2C_4H_2Fe_2(CO)_6$  (VI) does not appear to be possible from the available data.

Ultraviolet irradiation of aminoalkynes with  $Mn_2(CO)_{10}$  in tetrahydrofuran solution gave orange products of the stoichiometry (aminoalkyne) $Mn_2(CO)_8$ . The products of this type from  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and  $CH_3C\equiv CN(C_2H_5)_2$  were isolated in the pure state. An analogous orange liquid was also obtained from  $C_6H_5C\equiv CN(CH_3)_2$  and  $Mn_2(CO)_{10}$  which was shown by its  $\nu(CO)$  frequencies to be an analogous (aminoalkyne) $Mn_2(CO)_8$  derivative. However, this derivative could be purified neither by crystallization nor by evaporative vacuum distillation.

The involvement of the nitrogens of one of the dialkylamino groups in the ligand-metal bonding of these (aminoalkyne) $Mn_2(CO)_8$  derivatives is suggested by the failure to obtain a similar (alkyne) $Mn_2(CO)_8$  derivative from an analogous ultraviolet irradiation of 3-hexyne with  $Mn_2(CO)_{10}$ . Fur-

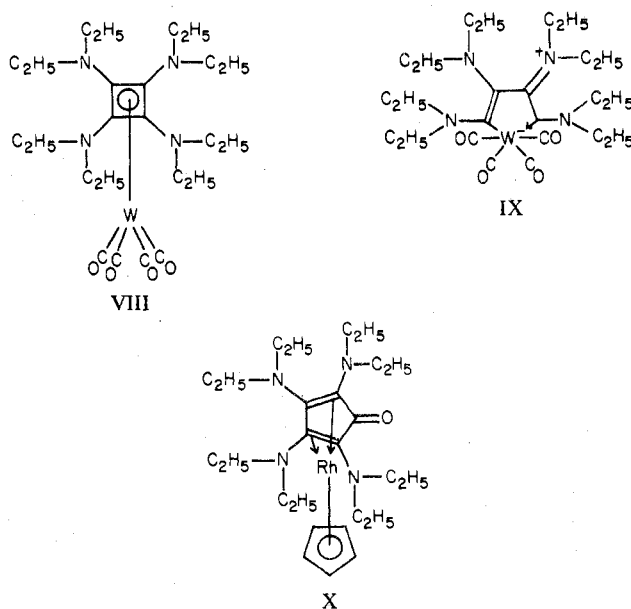
thermore, no manganese carbonyl derivatives containing only carbonyl and simple alkyne ligands appear to have been obtained.<sup>3,4</sup> A structure such as VII ( $R = CH_3$  or  $N(C_2H_5)_2$ )



with a  $\eta^3$ -CCN ligand and a rare gas electronic configuration for each manganese atom without a manganese-manganese bond is possible for (aminoalkyne) $Mn_2(CO)_8$  derivatives and is consistent with the observed spectroscopic data. The proton and carbon-13 NMR spectra of  $CH_3C_2N(C_2H_5)_2Mn_2(CO)_8$  both indicate nonequivalent ethyl groups suggesting that rotation around the carbon-nitrogen bond is impossible as in structure VII. The resonances at  $\delta$  232.9 and 136.8 in the carbon-13 NMR spectrum of  $CH_3C_2N(C_2H_5)_2Mn_2(CO)_8$  can be assigned to the carbons originating from the carbon-carbon triple bond in the original aminoalkyne. Again one of these carbon atoms has a relatively low-field chemical shift similar to that of aminocarbene complexes.

Ultraviolet irradiation of the diaminoalkyne  $(C_2H_5)_2N-C\equiv CN(C_2H_5)_2$  with  $W(CO)_6$  in tetrahydrofuran gave an orange product of stoichiometry  $[(C_2H_5)_2N]_4C_4W(CO)_4$ . Analogous products were not obtained from similar reactions of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with the other metal hexacarbonyls  $Mo(CO)_6$  and  $Cr(CO)_6$  or from reactions between aminoalkynes containing one amino group and  $W(CO)_6$ .

The infrared spectrum of  $[(C_2H_5)_2N]_4C_4W(CO)_4$  exhibits metal  $\nu(CO)$  frequencies corresponding to a *cis*- $L_2M(CO)_4$  pattern.<sup>17</sup> However, this compound cannot be the simple cyclobutadiene complex VIII for the following reasons: (1)



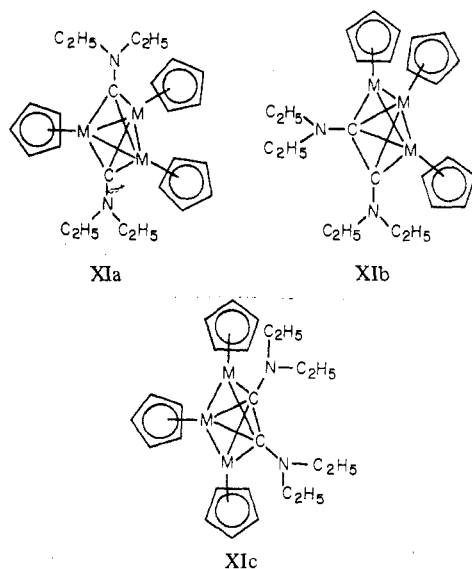
the carbon-13 NMR spectrum exhibits two pairs of resonances in the metal carbonyl region of approximately equal relative intensities indicating a *cis*- $LL'M(CO)_4$  derivative where the L and L' ligands must be appreciably different; (2) the proton and carbon-13 NMR spectra exhibit an extremely complex pattern of ethyl resonances which clearly requires a larger number of nonequivalent ethyl groups than would be present in the cyclobutadiene complex VIII and demand a structure with very low symmetry. A possible structure for  $[(C_2H_5)_2N]_4C_4W(CO)_4$  consistent with its observed spectroscopic

properties is IX. In this structure the tungsten atom has the favored rare gas electronic configuration and there are no unprecedented bonding features. The  $[(C_2H_5)_2N]_4C_4$  unit acts as a chelate ligand which bonds to the tungsten atom through the two end carbon atoms of the four-carbon chain arising from coupling of the two alkyne units. Since structure IX must have from five to eight nonequivalent ethyl groups depending upon the barriers to rotation around the carbon–nitrogen bonds, the observation of a minimum of 11 nonequivalent ethyl  $CH_2$  carbon atoms in the carbon-13 NMR spectrum of this complex indicates that at least two stereoisomers must be present. This system is too complex for detailed interpretation at the present time.

The reaction between the diaminoalkyne  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and  $C_5H_5Rh(CO)_2$  gave two new cyclopentadienylrhodium derivatives. One of these products was the orange crystalline cyclopentadienone derivative  $[(C_2H_5)_2N]_4C_4CORhC_5H_5$  (X) similar to other reported cyclopentadienylrhodium–cyclopentadienone derivatives.<sup>18</sup> If the rhodium coupling to the  $(C_2H_5)_2N$  protons and carbons is assumed to be negligible consistent with the number of intervening bonds, then both the proton and carbon-13 NMR spectra may be interpreted as indicating two types of nonequivalent ethyl groups in a 1:1 ratio consistent with structure X.

The second product obtained from  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and  $C_5H_5Rh(CO)_2$  was a black crystalline trimetallic derivative  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$ . The proton and carbon-13 NMR spectra of this complex indicate equivalence of the four ethyl groups. More significantly, in addition to the two ethyl and one cyclopentadienyl resonances, the carbon-13 NMR spectrum of  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$  exhibits only one other resonance: a very low-field ( $\delta$  280.6) very clean 1:3:3:1 quartet ( $J = 40$  Hz). This indicates rather dramatically that at least on the NMR time scale both carbon atoms from the alkyne triple bond are equivalent and equivalently situated in  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$  relative to each of the three rhodium atoms.

Three structures XIa, XIb, and XIc ( $M = Rh$ ) are possible



for  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$  with the three rhodium atoms and the two carbon atoms originating from the carbon–carbon triple bond of the diaminoalkyne situated at the five vertices of a trigonal bipyramid. Of these three structures, only structure XIa with the carbon atoms at both apices and not directly bonded to each other has both vertex carbon atoms both equivalent and equivalently situated with respect to each of the three rhodium atoms. Possible structures for  $(C_5-$

$H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$  based on polyhedra with five vertices which are both less symmetrical and less likely on the basis of recent views<sup>19,20</sup> on bonding in cluster compounds would have either nonequivalent vertex carbon atoms or nonequivalent relationships between the carbon atoms and the three rhodium atoms and thus are excluded by the carbon-13 NMR spectrum. Thus, the observation of a single symmetrical 1:3:3:1 quartet from the two carbons originating from the carbon–carbon triple bond uniquely indicates structure XIa for  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$ . The only conceivable alternative interpretation of the carbon-13 NMR spectrum of  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$  requires postulation of fluxional<sup>21</sup> properties with rapid interconversion between less symmetrical structures, possibly XIb and XIc, to make equivalent on an NMR time scale both the two cluster carbon atoms and the relationship between each carbon atom and each of the rhodium atoms. This less likely possibility is excluded by preliminary x-ray diffraction data<sup>22</sup> which support structure XIa for  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$ . The carbon–carbon triple bond in  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  has thus undergone complete cleavage to give individual  $(C_2H_5)_2NC$  carbyne units in its reaction with  $C_5H_5Rh(CO)_2$ .

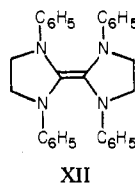
Reaction of  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  with  $C_5H_5Co(CO)_2$  gave a black crystalline solid  $(C_5H_5)_3Co_3C_2[N(C_2H_5)_2]_2$  which appears to have structure XIa ( $M = Co$ ) completely analogous to that of its rhodium analogue discussed above. The apical cluster carbon atoms in  $(C_5H_5)_3Co_3C_2[N(C_2H_5)_2]_2$  exhibit a single carbon-13 resonance with the very low-field chemical shift of  $\delta$  321. This resonance is broadened drastically relative to the other carbon-13 resonances, presumably because of interaction with the directly bonded spin  $7/2$  cobalt atoms.

## Discussion

The reactions of aminoalkynes with metal carbonyls discovered during this work appear to be of three different types: (1) oligomerization reactions to form metallacyclopentadiene or cyclopentadienone derivatives which involve only the carbon–carbon triple bond of the aminoalkyne; (2) reaction of the aminoalkyne in its keteneimmonium ylide form Ib which leads to products containing  $\eta^3$ -CCN ligands involving bonding of the original amino nitrogen as well as the original triple-bond carbons to the transition metal; (3) complete cleavage of the carbon–carbon triple bond to give metal complexes built from aminocarbyne units. Of these three reaction types only the first type (oligomerizations involving only the carbon–carbon triple bond) has a precedent in previously reported<sup>3,4</sup> alkyne metal carbonyl chemistry and in this work is exemplified by the cyclopentadienone complexes  $[(C_2H_5)_2N]_4C_4COFe(CO)_3$  (II:  $R = R' = N(C_2H_5)_2$ ),  $[(C_2H_5)_2N]_2(CH_3)_2C_4COFe(CO)_3$  (II:  $R = N(C_2H_5)_2$ ,  $R' = CH_3$ ), and  $[(C_2H_5)_2N]_4C_4CORhC_5H_5$  (X) as well as the tricarbonylferrole–iron tricarbonyl complex  $[(CH_3)_2N]_2C_4H_2Fe_2(CO)_6$  (VI:  $R = H$ ,  $R' = N(CH_3)_2$ ;  $R = N(CH_3)_2$ ,  $R' = H$ ). Reaction of the aminoalkyne as its keteneimmonium ylide form Ib is necessarily unique to aminoalkyne chemistry and in this work is exemplified by the complexes  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  (III),<sup>26</sup>  $C_6H_5C_2N(CH_3)_2Fe_2(CO)_6$  (IV), and  $RC_2N(C_2H_5)_2Mn_2(CO)_8$  (VII:  $R = CH_3$ ,  $N(C_2H_5)_2$ ) all containing ligands with  $\eta^3$ -CCN bonds to metal atoms. The tungsten complex  $[(C_2H_5)_2N]_4C_4W(CO)_4$  which appears to have structure IX with a chelating ligand can arise from an oligomerization reaction involving the keteneimmonium ylide form of the aminoalkyne.

The complete cleavage of the carbon–carbon triple bond in an alkyne to form metal complexes built from carbyne units as exemplified by the formation of  $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$  (XIa:  $M = Co, Rh$ ) from  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and  $C_5H_5M(CO)_2$  is completely unprecedented in alkynemetal

carbonyl chemistry. However, the carbon-carbon double bonds in certain substituted tetraaminoethylene derivatives such as XII can be cleaved by transition metal derivatives to



form the corresponding diaminocarbenemetal complexes.<sup>23</sup> Nitrogen atoms flanking carbon-carbon multiple bonds thus increase their susceptibility to cleavage by transition metal derivatives. The nitrogen lone pair can weaken carbon-carbon multiple bonds by partial residence in their antibonding orbitals as suggested by effective keteneimmonium ylide resonance structures Ib for aminoalkynes. Coordination of transition metals can also weaken carbon-carbon multiple bonds both by removal of electron density from bonding orbitals and by introduction of electron density into antibonding orbitals through retrodonative bonding. The  $C_5H_5M$  units ( $M = Co, Rh$ ) have relatively electron-rich metal atoms since they lack the strongly retrodonative bonding carbonyl groups. Therefore, they can donate electron density efficiently into carbon-carbon multiple-bond antibonding orbitals. The synergistic effects of the two amino groups and the three  $C_5H_5M$  ( $M = Co, Rh$ ) units in efficiently populating the carbon-carbon triple-bond antibonding orbitals in  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  during its reaction with  $C_5H_5M(CO)_2$  ( $M = Co, Rh$ ) to form  $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$  (XIa) are clearly sufficient to cause complete rupture of the carbon-carbon triple bond.

The formulations of  $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$  as the trigonal-bipyramidal metal-carbon clusters XIa ( $M = Co, Rh$ ) are clearly consistent with recently developed<sup>19,20</sup> rules of metal cluster structure. The  $C_5H_5Co$  unit is well known from carbollylmetal chemistry<sup>24</sup> to donate two electrons to a cage like a BH unit. The  $(C_2H_5)_2NC$  carbyne units must donate three electrons to a cage, at least in the absence of any possible but unprecedented effects involving the nitrogen lone pair. The trigonal-bipyramidal metal-carbon cages in the complexes  $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$  (XIa:  $M = Co, Rh$ ) thus contain  $(3 \times 2) + (2 \times 3) = 12$  electrons in accord with the  $2v + 2$  rule<sup>19,20</sup> where  $v$  is the number of vertices in the closed triangulated cluster. The compounds  $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$  (XIa:  $M = Co, Rh$ ) are thus boron-free analogues of the known<sup>25</sup> trigonal-bipyramidal carborane  $C_2B_3H_5$ .

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**Registry No.**  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ , 5323-13-7;  $C_6H_5C\equiv CN(CH_3)_2$ , 4604-65-3;  $CH_3C\equiv CN(C_2H_5)_2$ , 4231-35-0;  $HC\equiv CN(CH_3)_2$ , 24869-88-3;  $Fe(CO)_5$ , 13463-40-6;  $Fe_3(CO)_{12}$ , 17685-52-8;  $Mn_2(CO)_{10}$ , 10170-69-1;  $W(CO)_6$ , 14040-11-0;  $C_5H_5Co(CO)_2$ , 12078-25-0;  $C_5H_5Rh(CO)_2$ , 12192-97-1;  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$ , 58150-24-6;  $[(C_2H_5)_2N]_4C_4COFe(CO)_3$ , 58150-25-7;  $C_6H_5C_2-$

$N(CH_3)_2Fe_2(CO)_6$ , 58150-26-8;  $[(C_2H_5)_2N]_2(C_2H_5)_2C_4COFe(CO)_3$ , 58150-27-9; VI,  $R = H, R' = N(CH_3)_2$ , 58207-95-7;  $(C_2H_5)_2N-C_2N(C_2H_5)_2Mn_2(CO)_8$ , 58167-43-4;  $CH_3C_2N(C_2H_5)_2Mn_2(CO)_8$ , 58167-45-6;  $C_6H_5C_2N(CH_3)_2Mn_2(CO)_8$ , 58167-44-5;  $[(C_2H_5)_2N]_4C_4W(CO)_4$ , 58150-28-0;  $(C_5H_5)_3Co_3C_2[N(C_2H_5)_2]_2$ , 58150-29-1;  $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$ , 58150-30-4;  $[(C_2H_5)_2N]_4C_4CORhC_5H_5$ , 58150-31-5; VI,  $R = N(CH_3)_2, R' = H$ , 58207-96-8.

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- (26) **Note Added in Proof.** After this paper was accepted for publication, results from an x-ray crystallography study (R. C. Pettersen and G. Cash, private communication, Jan 1976) on the complex  $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$  became available. These preliminary results indicate structure IIIa for this complex rather than the structure III proposed in this paper. In the formation of IIIa from  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$  and iron carbonyls the carbon-carbon triple bond of the diaminoalkyne has been completely broken to form two bridging dialkylimmonioalkene ligands. Thus  $Fe(CO)_5$  like  $C_5H_5M(CO)_2$  ( $M = Co$  and  $Rh$ ) can cause complete cleavage of the carbon-carbon triple bond in  $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ .

