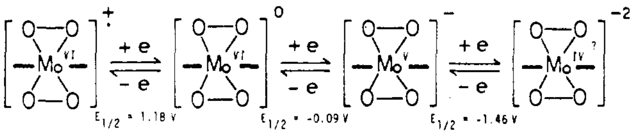
Scheme I



metrical bands. The intense absorption is attributed to the ^{96}Mo species, and the value of $g = 1.980$ closely approximates that for other complexes of OMo(TPP)X.[9,10] The expected hyperfine structure due to interactions with four nitrogen nuclei around the ^{96}Mo nucleus was not observed under our experimental conditions. The six weaker bands are assigned to the hyperfine structure caused by the interaction with ^{95}Mo and ^{97}Mo nuclei.

On the basis of coulometric, voltammetric, and spectroscopic data Scheme I may be assigned for $(O_2)_2$Mo(TmTP) oxidation–reduction in CH_2Cl_2 on the cyclic voltammetry time scale.

Attempts to spectrally identify the site of the second reduction (i.e., metal or ring based) were unsuccessful due to decomposition of $[(O_2)_2Mo(TmTP)]^{2-}$ at larger time scales of electrolysis. In all cases only $[TmTPH_2]^{2-}$ and some form of Mo^{IV} were obtained. Evidence for the latter oxidation state of Mo comes from cyclic voltammetry after bulk electrolysis that yielded a wave at 0.0 V, which is characteristic for a Mo^{IV}/Mo^{V} redox couple.

The interesting and significant aspect of the above mechanism is that reduction of $(O_2)_2$Mo(TmTP) appears to be at the central metal and not at the porphyrin ring. The alternate explanation of π-radical formation can be ruled out on the basis of the potential for Red(1) and the large separation between Red(1) and Red(2),[11] as well as by the nonradical spectrum illustrated in Figure 3b. This provides the first example where a peroxo-bound metalloporphyrin can be reduced at the central metal without affecting the nature of the metal–oxygen bond.

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Registry No. $(O_2)_2$Mo(TmTP), 87371-95-7; $[(O_2)_2Mo(TmTP)]^+$, 87371-96-8; $[(O_2)_2Mo(TmTP)]^-$, 87371-97-9.

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(11) All known tetraphenylporphyrin derivatives show ring reductions between −1.0 and −1.8 V vs. SCE, and the majority exhibit potential differences of 300–470 mV between $E_{1/2}$ values for formation of the anion radical and dianion.[8]

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Articles

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Synthesis of Chelating Bidentate and Tridentate Cyano Ligands and Their Complexes with Group 7 Metal Carbonyls

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Two new bidentate cyano ligands, DiCN-3 (**2**) and DiCN-4 (**3**) (α,ω-bis(2-cyanophenoxy)propane and -butane, respectively), have been prepared. These ligands and the ethane analogue DiCN-2 (**1**) react with $Mn(CO)_5Br$ to afford complexes of the composition $Mn(CO)_3$(DiCN-*n*)Br (*n* = 2, **9**; *n* = 3, **10**; *n* = 4, **11**). Complexes **9** and **10** appear to be mononuclear and contain 13- and 14-membered chelate rings, respectively. Ligand **3** in **11** might be either chelated or bridged. IR studies of the reaction between **1**–**3** and $Mn_2(CO)_6(CH_3CN)_2(\mu\text{-}Br)_2$ show that, under identical conditions, more nitrile groups of **1** than of **2** and **3** are bound to the $Mn(CO)_3Br$ unit; this results suggests that DiCN-2 is a better chelating ligand than DiCN-3 or DiCN-4. A novel tricyano ligand, TriCN (1,3,5-tris(2-cyanophenyl)benzene (**8**)) has been synthesized from 2-methylacetophenone. TriCN functions either as a bidentate ligand, as in $M(CO)_3$(TriCN)Br (M = Mn, **12**; M = Re, **14**), or as a tridentate ligand, as in $[M(CO)_3(TriCN)]PF_6$ (M = Mn, **13**; M = Re, **15**). Complexes **13** and **15** of TriCN are the first examples in which a tridentate cyano ligand chelates to a single metal center through its nitrogen lone pairs.

Introduction

Recently, we described the synthesis of bidentate cyano (DiCN) and isocyano (DiNC and *t*-BuDiNC) ligands, which were shown to form chelate complexes with a variety of low-valent transition metals.[1,2] The DiCN ligand of those studies is the first example of a dicyanide capable of chelation to a single metal through its nitrogen lone pairs. We report here the synthesis and reactions of two new bidentate cyano ligands, DiCN-3 and DiCN-4. These ligands are structurally similar to the previously reported DiCN ligand (hereafter referred to as DiCN-2 (**1**)). The three ligands vary only in *n*, the number of methylene units connecting the phenoxy oxygens, and should be capable of forming chelate rings containing 13 (DiCN-2) to 15 (DiCN-4) members. Also reported here is the synthesis of a novel tricyano ligand, TriCN (**8**), and several of its metal

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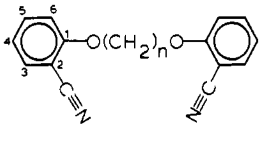
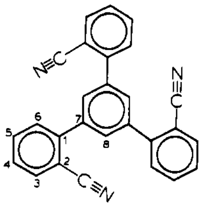


1, DiCN-2 ($n = 2$)
2, DiCN-3 ($n = 3$)
3, DiCN-4 ($n = 4$)



8, TriCN

complexes. Space-filling molecular models suggest that the TriCN ligand might be capable of acting as either a bidentate or tridentate chelating ligand, forming 12-membered chelate rings.

The goals of this research were to evaluate the effect of chelate ring size on the stability of DiCN-*n* complexes and to determine whether the tridentate ligand TriCN with a highly unusual and rigid structure was capable of forming metal complexes. The results discussed here represent part of a more general investigation into the synthesis and reactivity of polydentate cyano,[1,2] isocyano,[1-6] and diazonium[7] ligands.

Experimental Section

General Information. Dichloromethane and 1,2-dichloroethane were distilled from CaH_2 under N_2 before use; pyridine and *N*,*N*-dimethylformamide (DMF) were dried by distillation from CaO. AR grade anhydrous Et_2O was used as received. All other solvents were reagent grade products and were dried over 4-Å molecule sieves prior to use. The reagents $(Bu_4N)_2Cr_2O_7$,[8] $Mn(CO)_5Br$,[9] and $Re(CO)_5Br$[10] were prepared by the cited methods. DiCN-2 (1) and its Mn complex, *fac*-$Mn(CO)_3$(DiCN-2)Br (9), were synthesized as described previously.[1] All other reagents were obtained commercially and were used as received. Transition-metal complexes were prepared in Schlenkware or similar apparatus under N_2 with the use of standard inert-atmosphere techniques.[11] Routine infrared spectra were recorded on Perkin-Elmer 281 or 681 spectrophotometers calibrated against CO gas. Low-frequency infrared spectra were determined with an IBM IR 98 Fourier transform spectrometer. Proton (89.55 MHz) and ^{13}C NMR spectra were obtained on a JEOL FX90Q NMR spectrometer; chemical shifts are given in δ units downfield from tetramethylsilane. Mass spectra were obtained on a Finnigan 4000 or AEI MS902 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Ligand Syntheses. 1,3-Bis(2-cyanophenoxy)propane, DiCN-3 (2). A solution of 2-cyanophenol (4.78 g, 40.1 mmol) in 20 mL of DMF was added dropwise to a stirred suspension of NaH (0.96 g, 40 mmol) in 10 mL of DMF at 80 °C under N_2. After 3 h, most of the NaH had dissolved and 2.0 mL (4.0 g, 20 mmol) of 1,3-dibromopropane was added. The mixture was then heated to 120 °C. This temperature was maintained for 6 h, and the reaction was cooled to room temperature. The mixture was poured into 100 mL of well-stirred ice water. The slurry was filtered, and the solid was washed with water (6 × 30 mL) and cold MeOH (3 × 10 mL) and dried in vacuo to give **2** (3.0 g, 53%) as a white powder. An analytical sample, mp 113–115 °C, was obtained by recrystallization from a minimum amount of hot $CHCl_3$. Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 74.17; H, 5.51; N, 10.18. ^1H NMR ($CDCl_3$): δ 7.64–6.90 (m, ArH), 4.34 (t, $J = 5.8$ Hz, OCH_2); 2.39 (pentet, $J = 5.8$ Hz, CH_2). ^{13}C NMR ($CDCl_3$): 160.2 (C1), 101.8 (br, C2), 133.4 (C3), 120.8 (C4), 134.4 (C5), 112.3 (C6), 116.3 (br, CN), 64.7 (OCH_2), 28.6 ppm (CH_2).

1,4-Bis(2-cyanophenoxy)butane, DiCN-4 (3). In a procedure identical with that described for the synthesis of DiCN-3, reaction of 2-cyanophenol (4.8 g, 40 mmol), NaH (0.96 g, 40 mmol), and 1,4-dibromobutane (2.4 mL, 4.3 g, 20 mmol) yielded 2.5 g (43%) of the crude product. Recrystallization from hot $CHCl_3$ gave colorless crystals, mp 151–153 °C. Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.27; H, 5.89; N, 9.48. ^1H NMR ($CDCl_3$): δ 7.62–6.90 (m, ArH), 4.21 (m, OCH_2), 2.12 (m, CH_2CH_2). ^{13}C NMR ($CDCl_3$): 160.7 (C1), 102.0 (br, C2), 133.7 (C3), 120.8 (C4), 134.4 (C5), 112.4 (C6), 116.5 (br, CN), 68.7 (OCH_2), 25.8 ppm (CH_2CH_2).

1,3,5-Tris(2-methylphenyl)benzene (4). The method of Wirth et al.[12] was used to convert 25 g (0.19 mol) of 2-methylacetophenone to its diethyl ketal. In a modification of the literature procedure for the cyclocondensation of this ketal,[12] the whole sample of the distilled ketal was dissolved in 100 mL of dry C_6H_6 at 25 °C, and HCl(g) was passed through the solution for 1 h. Rotary evaporation of the deep purple mixture gave a thick, orange oil, which was diluted with ca. 10 mL of C_6H_6 and immediately chromatographed on a 44 mm × 80 cm silica gel column prepared with CCl_4/hexane (2:1). With use of this solvent mixture, **4** eluted first as a pale yellow band. Solvent was removed by rotary evaporation, and the crude product was digested for 1 h in 150 mL of boiling EtOH. After the mixture was cooled to −20 °C, the product was filtered off, washed with EtOH at −20 °C, and dried in vacuo. This gave **4** as a colorless, microcrystalline solid: mp 130–134 °C (lit.[12] mp 134–135 °C); yield 9.82 g, 45%. ^1H NMR ($CDCl_3$): δ 7.27 (s, ArH), 7.26 (s, ArH), 2.37 (s, CH_3). ^{13}C NMR ($CDCl_3$): 141.8, 141.6, 135.4, 130.4, 130.0, 128.6, 127.3, and 125.9 (Ar), 20.7 ppm (CH_3).

1,3,5-Tris(2-(bromomethyl)phenyl)benzene (5). The following reaction was carried out as for the reported bromination of 2,11-dimethylbenzo[*c*]phenanthrene.[13] In a typical preparation, 9.50 g (27.3 mmol) of **4** was dissolved in 200 mL of degassed CCl_4, *N*-bromosuccinimide (15.10 g, 83.9 mmol) was added, and the mixture was heated to a gentle reflux. The addition of 0.1 g of benzoyl peroxide in 2 mL of $CHCl_3$ initiated the reaction. After refluxing for 1.5 h, the reaction mixture was cooled to room temperature, and the succinimide byproduct was removed by filtration. Carbon tetrachloride was removed on a rotary evaporator to give a yellow oil. This oil was stirred for 1 h with 20 mL of CCl_4/C_6H_6 (9:1 by volume) to precipitate **5** as a white powder. The mixture was stored at −20 °C overnight. The product was filtered off, washed with a small amount of the cold solvent mixture, and then dried in vacuo. The yield of **5** was 9.28 g (58%), mp 133–139 °C. Anal. Calcd for $C_{27}H_{21}Br_3$: C, 55.42; H, 3.62. Found: C, 55.64; H, 4.18. ^1H NMR ($CDCl_3$): δ 7.53–7.33 (m, ArH), 4.58 (s, CH_2). ^{13}C NMR ($CDCl_3$): 141.6, 140.4, 135.4, 130.9, 130.5, 128.7, and 128.3 (Ar), 32.3 ppm (CH_2).

1,3,5-Tris(2-formylphenyl)benzene (6). A mixture consisting of 8.94 g (15.3 mmol) of **5**, 21.52 g (30.74 mmol) of $(Bu_4N)_2Cr_2O_7$, and 35 mL of $CHCl_3$ was heated at reflux for 4 h. The green-black mixture was cooled to room temperature and poured onto 120 g of silica gel contained in a chromatography column 74 mm in diameter. The product was washed off the column with 2 L of Et_2O. Evaporation of the solvent and recrystallization of the residue from hot EtOH (washing with EtOH at −20 °C) gave **6** as a light yellow solid: mp 166–168 °C; yield 3.72 g, 62%. In Nujol mull, **6** exhibits two $\nu(C{=}O)$ bands, rather than one, at 1706 (s, sh) and 1690 cm^{-1} (s). A single, strong $\nu(C{=}O)$ absorbance is observed in $CHCl_3$ solution at 1695 cm^{-1}. Anal. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 83.27, H, 4.97. ^1H NMR ($CDCl_3$): δ 10.14 (s, CHO), 8.04 (m, ArH), 7.67–7.49 (m, ArH). ^{13}C NMR ($CDCl_3$): 191.6 (CHO), 144.1, 138.6,

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133.8, 131.0, and 128.5 ppm (Ar). ^{13}C NMR (CDCl$_3$/Me$_2$SO-d_6, 1:1): 189.8 (CHO), 142.2, 136.4, 131.9, 129.4, 129.1, 126.5, and 126.3 ppm (Ar).

1,3,5-Tris[2-((hydroxyimino)formyl)phenyl]benzene (7). A solution of **6** (3.47 g, 8.87 mmol) and NH$_2$OH·HCl (2.47 g, 35.5 mmol) in a mixture of EtOH (20 mL) and pyridine (20 mL) was refluxed for 6 h. The solvents were removed by short-path distillation at atmospheric pressure, followed by vacuum drying of the residue. Trituration of the resulting pale yellow oil with 15 mL of cold H$_2$O gave **7** as a white solid, which was isolated by filtration and washed with cold H$_2$O (2 × 15 mL) and cold EtOH (2 × 10 mL). The product was dried in vacuo for 12 h: yield 3.80 g (98%); mp 222–228 °C. Anal. Calcd for C$_{27}$H$_{21}$N$_3$O$_3$: C, 74.47; H, 4.86; N, 9.65. Found: C, 75.25; H, 5.23; N, 9.62. ^{1}H NMR (CD$_3$CN): δ 8.90 (s, br, OH), 8.14 (s, CH of *E* isomer[14]); 7.88 (m, ArH); 7.51–7.28 (m, ArH and CH of *Z* isomer[14]).

1,3,5-Tris(2-cyanophenyl)benzene, TriCN (8). A solution of **7** (3.66 g, 8.39 mmol) in 55 mL of distilled pyridine was cooled to 0 °C under N$_2$. The addition of MeSO$_2$Cl (5.0 mL, 7.3 g, 64 mmol) caused a color change to yellow and the precipitation of a white solid. The mixture was stirred 12 h at 30 °C and then cooled in ice to 0 °C. Water (150 mL) was slowly added to the cool solution, precipitating the crude product as a tan powder. This solid was isolated by filtration and washed with H$_2$O (3 × 20 mL) and then cold (0 °C) EtOH (3 × 10 mL). After being dried in vacuo, the product was dissolved in CHCl$_3$; the solution was treated with activated charcoal and filtered through an 8-mm layer of silica gel in a 60-mL fritted funnel in air. The volume of the solution was reduced to 40 mL, and ca. 40 mL of Et$_2$O was layered on the top of the solution, yielding, after 24 h, some yellowish crystals and a white solid. Another 20 mL of Et$_2$O was slowly added, and the solution was allowed to stand at −20 °C for 24 h. The resulting solids were filtered off, washed with 20 mL of Et$_2$O, and dried. Another recrystallization was carried out by slowly adding 80 mL of warm (45 °C) EtOH to a warm CHCl$_3$ solution of the product, followed by slow cooling to −20 °C. The yield of white to pale yellow microcrystals of **8** was 2.36 g (77%); mp 266–268 °C. Mass spectrum: M$^+$ *m/e* 381.1 (base). Anal. Calcd for C$_{27}$H$_{15}$N$_3$: C, 85.02; H, 3.96; N, 11.02. Found: C, 84.88; H, 4.06; N, 10.93. Other supporting data are presented in Tables I–III.

Preparation of Complexes. *fac*-Mn(CO)$_3$(DiCN-3)Br (10). Mn(CO)$_5$Br (0.104 g, 0.378 mmol) and DiCN-3 (0.105 g, 0.377 mmol) were dissolved in 10 mL of CHCl$_3$, and in darkness, the solution was refluxed for 1.3 h. After the mixture was cooled, it was filtered with the apparatus, being protected from light by aluminum foil. Solvent was removed at reduced pressure, and the resulting yellow solid was triturated twice with 10 mL of Et$_2$O, followed each time by decantation of the Et$_2$O solution. The remaining solid was dried in vacuo and scraped from the Schlenk tube to give **10** as a yellow microcrystalline solid: 0.087 g (46%); mp 100–110 °C (dec). Anal. Calcd for C$_{20}$H$_{14}$BrMnN$_2$O$_5$: C, 48.23; H, 2.84; N, 5.63. Found: C, 48.14; H, 3.09; N, 5.50.

***fac*-Mn(CO)$_3$(DiCN-4)Br (11).** In a procedure similar to that described for the DiCN-3 analogue, DiCN-4 (0.175 g, 0.60 mmol) and Mn(CO)$_5$Br (0.165 g, 0.60 mmol) were refluxed together in a CH$_2$Cl$_2$ solution (46 mL) in the dark for 9 h. (An IR spectrum of the solution after 1 h had revealed the presence of a small amount of Mn(CO)$_5$Br.) The cooled solution was taken to dryness and evaporated. Trituration with Et$_2$O (10 mL) and then pentane (10 mL) gave **11** as a yellow microcrystalline solid: 0.178 g (58%); mp 122–125 °C. Anal. Calcd for C$_{21}$H$_{16}$BrMnN$_2$O$_5$: C, 49.34; H, 3.15; N, 5.48. Found: C, 48.96; H, 3.34; N, 5.35.

***fac*-Mn(CO)$_3$(TriCN)Br (12).** TriCN (0.261 g, 0.684 mmol) and Mn(CO)$_5$Br (0.252 g, 0.916 mmol) were refluxed together in CH$_2$Cl$_2$ solution (35 mL) for 3.5 h in subdued light. After cooling, the reaction solution was filtered and evaporated to leave a yellow residue of the product and Mn(CO)$_5$Br. The latter was removed by four extractions with Et$_2$O (10 mL each), and the remaining solid was collected on a frit and dried in vacuo. This yielded 0.215 g (52%) of **12** as a yellow powder, mp 159–162 °C. Anal. Calcd for C$_{30}$H$_{15}$BrMnN$_3$O$_3$: C, 60.02; H, 2.52; N, 7.00. Found: C, 59.64; H, 3.03; N, 6.88.

***fac*-[Mn(CO)$_3$(TriCN)]PF$_6$ (13).** Halide abstraction from **12** (0.067 g, 0.111 mmol) was accomplished by the addition of AgPF$_6$ (0.0282 g, 0.112 mmol) in 7 mL of 1,2-C$_2$H$_4$Cl$_2$ to a solution of **12** in 3 mL of the same solvent. After the mixture was stirred for 20 min, AgBr was filtered off. The volume of the now pale yellow solution was reduced to half, and Et$_2$O was added until a slight turbidity developed. After the mixture was allowed to stand at 0 °C for 2 days, the mother liquor was decanted away and the product dried in vacuo, giving 0.018 g (24%). Complex **13** is a yellow microcrystalline solid that melts at 172–179 °C and then loses CO and resolidifies at 189 °C. Anal. Calcd for C$_{30}$H$_{15}$F$_6$MnN$_3$O$_3$P: C, 54.15; H, 2.27; N, 6.32. Found: C, 53.12; H, 2.58; N, 6.12.

***fac*-Re(CO)$_3$(TriCN)Br (14).** TriCN (0.0377 g, 0.099 mmol) and Re(CO)$_5$Br (0.0408 g, 0.100 mmol) were dissolved in 8 mL of 1,2-C$_2$H$_4$Cl$_2$, and the solution was refluxed for 5 h. Dichloroethane was removed at reduced pressure. Dichloromethane (2 mL) was added to the pale yellow gummy residue to dissolve it; then hexane was added with agitation until the turbidity of the solution persisted. The solution was filtered and allowed to stand at −20 °C for 3 days. This produced a single lump of light yellow crystals, which were washed with hexane, dried, and weighed 0.0718 g (89%). An analytical sample was obtained by preparative TLC (silica gel/CHCl$_3$) in air. The pure product was washed from the silica gel with CH$_2$Cl$_2$, precipitated from a concentrated CH$_2$Cl$_2$ solution with hexane, and dried for 24 h in vacuo. The colorless solid melted at 190–195 °C. The mass spectrum of **14** showed weak peaks assignable to the parent ion [Re(CO)$_3$(TriCN)Br]$^+$ at *m/e* 729, 731, and 733, corresponding to ^{185}Re^{79}Br, ^{185}Re^{81}Br (and ^{187}Re^{79}Br), and ^{187}Re^{81}Br, respectively. Anal. Calcd for C$_{30}$H$_{15}$BrN$_3$O$_3$Re: C, 49.25; H, 2.07; N, 5.74. Found: C, 48.95; H, 2.30; N, 5.58.

***fac*-[Re(CO)$_3$(TriCN)]PF$_6$ (15).** A solution of Re(CO)$_3$(TriCN)Br was prepared by heating TriCN (0.094 g, 0.246 mmol) and Re(CO)$_5$Br (0.100 g, 0.246 mmol) in 40 mL of 1,2-C$_2$H$_4$Cl$_2$ at 75 °C for 9.5 h. The volume of the solution was reduced to ca. 5 mL. While the solution was stirred, AgPF$_6$ (0.0645 g, 0.255 mmol) in 6 mL of CH$_2$Cl$_2$ was added, causing the precipitation of AgBr. After 15 min, an IR spectrum showed the reaction to be complete, and the reaction mixture was filtered. Evaporation of the solvents gave a pale yellow gum. This residue was taken up in 3 mL of CH$_2$Cl$_2$, and 4 mL of hexane was layered on top of this. After the mixture was allowed to stand for 5 days at −20 °C, some white crystals and a dirty amorphous solid had precipitated. The crystals were easily isolated, washed with hexane, and dried in vacuo for 6 days. The yield of **15** was 0.084 g (43%); mp 251–260 °C. A further crop of the product (0.036 g, 18%) was obtained by addition of 13 mL of hexane to the mother liquor and storing the solution at −20 °C for 5 days; total yield 0.120 g, 61%. Anal. Calcd for C$_{30}$H$_{15}$F$_6$N$_3$O$_3$PRe: C, 45.23; H, 1.90; N, 5.27. Found: C, 45.34; H, 2.02; N, 5.21.

Results and Discussion

Ligand Syntheses. The dicyano ligands **1–3** are prepared simply by displacement of the halide ions from the appropriate α,ω-dihaloalkane by sodium 2-cyanophenoxide in DMF solution. All three ligands are colorless, odorless solids. The ethane- and butane-bridged ligands (**1** and **3**, respectively) are moderately soluble in CHCl$_3$ and CH$_2$Cl$_2$ and sparingly soluble in Et$_2$O, benzene, and saturated hydrocarbons. The DiCN-3 ligand (**2**) has considerably greater solubility (ca. 10 times) in chlorinated solvents than do **1** and **3** but still very low solubilities in the less polar solvents. Infrared stretching frequencies of the cyano groups of **1–3** at 2231–2232 cm^{-1} (CHCl$_3$ solution) are slightly lower than that of C$_6$H$_5$CN (2235 cm^{-1}) in the same solvent.

The tricyano ligand, TriCN (**8**), is synthesized by the reaction sequence shown in Scheme I. In the first step, 2-methylacetophenone is converted to its diethyl ketal by reaction with HC(OEt)$_3$. Subsequent treatment with HCl(g) forms the condensation product **4**, which has been previously synthesized by this route.[12] Bromination with *N*-bromosuccinimide gives tribromide **5** in 58% yield. Further oxidation of the α-carbon with CHCl$_3$-soluble (Bu$_4$N)$_2$Cr$_2$O$_7$[8] to the trialdehyde, **6**, followed by oximation with NH$_2$OH·HCl/C$_5$H$_5$N affords trioxime **7**. Dehydration of **7** by MeSO$_2$Cl[15] gives

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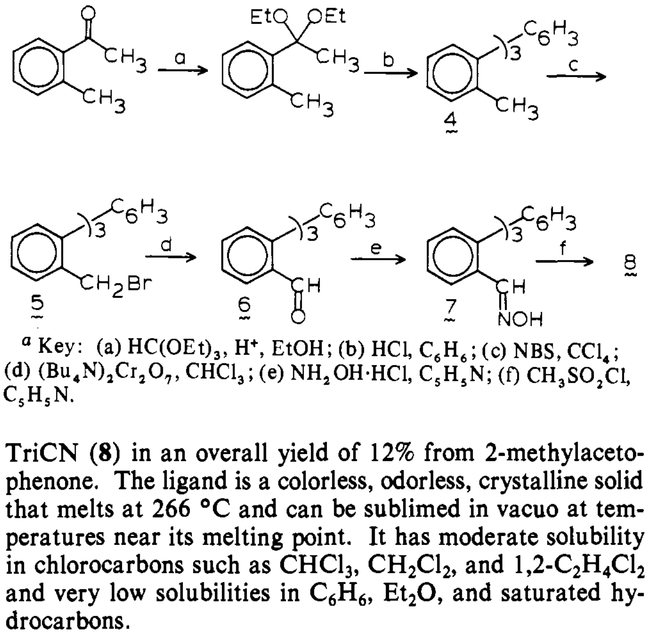
Table I. Infrared Data (cm^{-1}) for Cyano Ligands and Complexes[a]

compd	$\nu(N\equiv C)$	$\nu(C\equiv O)$
DiCN-2 (1)	2232	
DiCN-3 (2)	2231	
DiCN-4 (3)	2231	
TriCN (8)	2228	
fac-$Mn(CO)_3$(DiCN-2)Br (9)	2270 w	2044 s, 1968 s, 1938 s
fac-$Mn(CO)_3$(DiCN-3)Br (10)	2272 w	2044 s, 1973 s, 1942 s
b,c	2272 w	2042 s, 1960 s, 1936 s
fac-$Mn(CO)_3$(DiCN-4)Br (11)	2272 w	2050 s, 1972 s, 1944 s
b,d	2269 w	2044 s, 1974 s, sh, 1959 s, 1944 s, 1896 sh
fac-$Mn(CO)_3$(TriCN)Br (12)	2267 vw, 2228 w	2046 s, 1972 s, 1941 s
fac-[$Mn(CO)_3$(TriCN)]PF_6 (13)[b]	2268 w	2066 s, 1986 s
fac-$Re(CO)_3$(TriCN)Br (14)	2268 vw, 2228 w	2039 s, 1950 s, 1916 s
fac-[$Re(CO)_3$(TriCN)]PF_6 (15)[b]	2267 w	2052 s, 1951 s, br
fac-$Mn(CO)_3(CH_3CN)_2Br$[b,e]	2302 vw, 2276 w[f]	2043 s, 1957 s, 1934 s
fac-[$Mn(CO)_3(CH_3CN)_3$]PF_6[g]	2328, 2300[f]	2060 s, 1982 s
fac-[$Re(CO)_3(CH_3CN)_3$]PF_6[g]	2325, 2296[f]	2045 s, 1956 s

[a] In $CHCl_3$ solution unless otherwise noted. [b] Nujol mull. [c] Low-frequency bands at 676 s, 628 s, 590 w, sh, 525 m, 498 s, 464 m, sh, 402 w, br, 285 vw, br, 200 vw. [d] Low-frequency bands at 678 s, 633 s, 626 s, 600 w, 594 w, 567 w, 526 m, 515 m, sh, 496 s, 478 m, 464 w, sh, 288 w, sh, 268 w, 198 w, sh, 186 w. [e] Reference 17. [f] Combination band $\delta_{sym}(CH_3) + \nu_{sym}(CC)$.[19] [g] Reference 22; $\nu(N\equiv C)$ in Nujol mull; $\nu(C\equiv O)$ in $CHCl_3$ solution.

Scheme I[a]



[a] Key: (a) $HC(OEt)_3$, H^+, EtOH; (b) HCl, C_6H_6; (c) NBS, CCl_4; (d) $(Bu_4N)_2Cr_2O_7$, $CHCl_3$; (e) $NH_2OH\cdot HCl$, C_5H_5N; (f) CH_3SO_2Cl, C_5H_5N.

Table II. ^1H NMR Data of TriCN and Its Re Complexes

compd	solvent	δ(ArH)
TriCN	CD_3CN	7.94 s, 7.89–7.50 m
TriCN	$CDCl_3$	7.89 s, 7.83–7.44 m
14	$CDCl_3$	8.00–7.42 m
15	CD_3CN	8.06–7.49 m, 7.45 s

TriCN (**8**) in an overall yield of 12% from 2-methylacetophenone. The ligand is a colorless, odorless, crystalline solid that melts at 266 °C and can be sublimed in vacuo at temperatures near its melting point. It has moderate solubility in chlorocarbons such as $CHCl_3$, CH_2Cl_2, and 1,2-$C_2H_4Cl_2$ and very low solubilities in C_6H_6, Et_2O, and saturated hydrocarbons.

DiCN Complexes. The DiCN ligands **1**–**3** react with $Mn(CO)_5Br$ over a period of several hours in refluxing $CHCl_3$ or CH_2Cl_2 with the liberation of CO to afford the derivatives *fac*-$Mn(CO)_3$(DiCN-*n*)Br (*n* = 2, **9**[2]; *n* = 3, **10**; *n* = 4, **11**). The low yields of the last two compounds (46% and 58%, respectively) are due in part to the photosensitivity of such bis(organocyanide) derivatives of $Mn(CO)_5Br$[16] (vide infra). The facial geometries of the complexes are supported by solution IR spectra (Table I), which show the characteristic pattern of three strong $\nu(C\equiv O)$ absorptions expected for tricarbonyl complexes with C_s symmetry at 2042–2050, 1968–1973, and 1938–1944 cm^{-1} ($CHCl_3$). These bands are close to those reported for *fac*-$Mn(CO)_3(CH_3CN)_2Br$[17] (Table I). In the region 2300–2200 cm^{-1}, the complexes exhibit a single, weak $\nu(N\equiv C)$ band at ca. 2270 cm^{-1}, assigned to the metal-bound cyano groups. Single, weak, high-frequency $\nu(N\equiv C)$ bands are commonly observed for coordinated RCN groups in a large number of complexes.[18] To avoid confusion, it should be noted that, of the two high-frequency bands observed for the acetonitrile complex in Table I (and others[19]), the one of lower frequency is the combination band, $\delta_{sym}(CH_3) + \nu_{sym}(CC)$,[19] and not a cyano group mode.

While the solution IR spectra of all three complexes are similar, there are some differences between the solid-state IR spectrum of **11** and those of **9** and **10**. In the $\nu(C\equiv O)$ region, **11** exhibits "extra" shoulders at 1974 and 1896 cm^{-1}. Three additional bands are observed also in the region 680–460 cm^{-1}, relative to **10** (Table I). These additional bands might be due to either solid-state splitting or the existence of **11** as a (DiCN-4)-dibridged dimer of C_{2v} symmetry or a polymer, for which up to five IR-active $\nu(C\equiv O)$ bands are expected. Thus, there is some question about the structure of the DiCN-4 complex, **11**.

In ambient room light, $CHCl_3$ or CH_2Cl_2 solutions of **9**–**11** begin to precipitate a white solid within minutes of preparation. This process is accompanied by the liberation of the free DiCN-*n* ligand and more complicated changes in the $\nu(C\equiv O)$ region of the IR spectrum. The ultimate products obtained via sunlight photolysis (20 min) of these complexes are free ligand, CO, and, presumably, manganous halide(s). Bamford and co-workers[16] have previously described a similar photodecomposition of $Mn(CO)_3(CH_3CN)_2Br$ (and $Mn(CO)_5Br$) in C_6H_6 solution to give $Mn_2(CO)_{10}$ as the major identified product. Unfortunately, this photodecomposition reaction precluded the measurement of well-resolved NMR spectra for **9**–**11**, due to the generation of paramagnetic Mn(II) salts. Molecular weight measurements, which might distinguish between mono- and polynuclear structures for **11**, were discouraged by this decomposition as well. When dissolved in neat $(CH_3)_2CO$, the DiCN-*n* complexes **9**–**11** are solvolyzed within minutes to $\{Mn(CO)_3[(CH_3)_2CO]_3\}Br$, identified by its IR spectrum.[20,21]

It was of interest to evaluate the relative metal-binding abilities of the DiCN-*n* ligands. A suitable starting material

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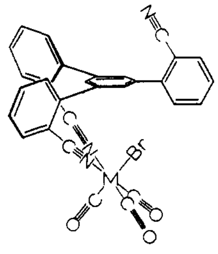
Table III. ^{13}C NMR Data (ppm) for TriCN and Its Re Complexes[a,b]

compd	1	2	3	4	5	6	7	8	CN	CO
TriCN[c]	144.2	111.3	133.5	130.6	133.9	129.5	139.1	128.3	118.7	...
TriCN[d]	144.5	111.8	133.7	130.8	134.2	129.9	139.6	128.7	119.0	...
Re(CO)$_3$(TriCN)Br[c]	143.7	111.3	133.4	131.2	133.6	130.3	138.6	128.7	118.7	191.5
	146.1	108.7	134.1		134.9		140.6		120.9	
[Re(CO)$_3$(TriCN)]PF$_6$[d]	147.8	111.0	132.8	129.8	135.7	129.4	140.0	129.0	121.4	193.9

[a] Chemical shifts assigned by comparison with spectrum calculated according to ref 24. [b] Where two data are presented for one C atom, the upper one is of lower intensity (ca. 1:2) and is assigned to an atom associated with the uncoordinated portion of the ligand. [c] CDCl$_3$ solvent. [d] CD$_2$Cl$_2$ solvent.

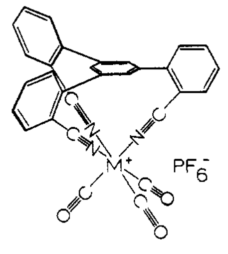
for such studies was the dimer $Mn_2(CO)_6(CH_3CN)_2(\mu\text{-}Br)_2$.[19] Bamford et al.[16] previously demonstrated the existence of the equilibrium $Mn_2(CO)_6(CH_3CN)_2(\mu\text{-}Br)_2 + 2CH_3CN \rightleftarrows 2Mn(CO)_3(CH_3CN)_2Br$. On the basis of this reaction, it is likely that a major product formed in the reaction between $Mn_2(CO)_6(CH_3CN)_2(\mu\text{-}Br)_2$ and a DiCN ligand is mononuclear Mn(CO)$_3$(DiCN-*n*)Br. A measure of the relative chelating abilities of the DiCN ligands might then be given by the amount of DiCN ligand that is bound to the metal at equilibrium. Rapid reactions occurred between the dimer and each of the DiCN ligands in CHCl$_3$ solution in the dark. From an initial concentration of 0.014 M $Mn_2(CO)_6(CH_3CN)_2(\mu\text{-}Br)_2$ and 0.027 M DiCN, a mixture of products was formed, as shown by IR analysis in the region 2300–2200 cm^{-1}; bands corresponding to coordinated DiCN-*n* (ca. 2270 cm^{-1}), free DiCN-*n* (2231–2232 cm^{-1}), and free CH$_3$CN (ca. 2250 cm^{-1}) were observed. From the intensity of the free DiCN-*n* absorption, the percentage of the total DiCN-*n* that was uncoordinated was calculated: DiCN-2, 8 ± 1%; DiCN-3, 14 ± 1%; DiCN-4, 14 ± 1%. These data suggest that the DiCN-2 ligand competes somewhat more effectively for coordination sites at the Mn center than do DiCN-3 and DiCN-4. It therefore appears that DiCN-2 forms more stable chelates than DiCN-3 or DiCN-4. The lower conformational flexibility of DiCN-2 than of DiCN-3 and DiCN-4, as indicated by molecular models, also indicates that DiCN-2 would be expected to be the best chelating ligand in this series.

TriCN Complexes. The neutral, six-coordinate *fac*-Mn(CO)$_3$(TriCN)Br (**12**) is formed upon reaction of TriCN with a 35% excess of Mn(CO)$_5$Br in refluxing CH$_2$Cl$_2$ over a period of 3.5 h and is isolated in 52% yield. The Re analogue, **14**, is obtained in 89% yield from the reaction of TriCN with an equimolar amount of Re(CO)$_5$Br in refluxing 1,2-C$_2$H$_4$Cl$_2$ (5 h). Complexes **12** and **14** each contain TriCN as a bidentate ligand and should possess local coordination geometries similar to those of complexes **9**–**11**. Accordingly, infrared spectra of **12** and **14** in CHCl$_3$ solution (Table I) each show three strong ν(C≡O) bands. Also in support of bidentate coordination of TriCN in **12** and **14** is the observation of two ν(N≡C) bands corresponding to free (2228 cm^{-1}, weak) and coordinated (2268 cm^{-1}, very weak) cyano groups. That coordinated cyano group ν(N≡C) bands are often of lower intensity than that of the free ligand has already been noted.[18] Like its DiCN analogues, complex **12** is photosensitive, decomposing rapidly in light-exposed chlorocarbon solutions. The Re analogue, **14**, however, is stable with respect to this type of decomposition.



12, M = Mn
14, M = Re

The neutral, bidentate complexes **12** and **14** are converted to the cationic tridentate complexes *fac*-[M(CO)$_3$(TriCN)]PF$_6$ (M = Mn, **13**; M = Re, **15**) upon treatment with AgPF$_6$ in 1,2-C$_2$H$_4$Cl$_2$ solution. In these reactions, coordinated bromide ion is removed from the Mn or Re center by Ag$^+$; the open coordination site is then occupied by the remaining cyano group of the TriCN ligand. Complexes **13** and **15** are expected on the basis of molecular models to have either C_{3v} or C_3 symmetry. The observation of strong ν(C≡O) bands (of A$_1$ and E symmetry in C_{3v}) for each complex supports this expectation. The CH$_3$CN analogues $[M(CO)_3(CH_3CN)_3]^+$ (M = Mn, Re[22,23]) exhibit similar IR spectra (Table I). Treatment of the Mn cation, **13**, with an equimolar amount of Et$_4$NBr in CH$_2$Cl$_2$ leads to the total disappearance of **13** and the formation of **12** over a period of 2 h.



13, M = Mn
15, M = Re

The stability of both Re complexes, **14** and **15**, has allowed the measurement of well-resolved ^{1}H NMR (Table II) and ^{13}C NMR (Table III) spectra. The ^{1}H NMR spectrum of free TriCN (Table II) includes a sharp, low-field singlet at 7.94 ppm (CD$_3$CN) in addition to the complicated multiplet of the aromatic protons at slightly higher field. This singlet integrates to roughly three protons and is assigned to the three chemically equivalent protons residing on the central phenyl ring of the ligand. The ^{1}H NMR spectrum of the bidentate complex **14** consists of a multiplet from which the previously observed spike is absent. In the ^{1}H NMR spectrum of the symmetrical tridentate complex **15**, the sharp, three-proton spike reappears as a high-field singlet at 7.45 ppm (CD$_3$CN). The variance in chemical shift of these protons from that of free TriCN probably arises from magnetic anisotropic effects of the peripheral phenyl and/or cyano groups, which would be much different in the relatively flat free ligand than in the near-C_{3v} structure of complex **15**.

In ^{13}C NMR studies, the free TriCN ligand exhibits nine signals, one for each group of three symmetry-related carbon atoms. When it is complexed as a bidentate ligand to rhenium in **14**, 15 signals are observed. In this case, all but three of the ligand carbon resonances are split into two signals in a 1:2 intensity ratio. Furthermore, each of those with the lower intensity has a chemical shift that falls within 0.5 ppm of the corresponding resonance in free TriCN. The higher intensity signal of each 1:2 pair is shifted by 0.7–2.4 ppm from the

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corresponding resonance in the free ligand. In the cationic, fully chelated complex **15**, the ^{13}C NMR pattern of the ligand is seen as another simple nine-line pattern, as is required by either the C_3 or C_{3v} symmetry of this complex.

The synthesis and characterization of complexes **13** and **15** demonstrate the ability of TriCN to act as a facially coordinating tridentate ligand. Other TriCN-type ligands, such as those with isocyano rather than cyano donor groups, would also be expected to form stable metal complexes. Such octahedral complexes with two TriCN-type ligands would have especially interesting geometries.

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Registry No. **2**, 87226-86-6; **3**, 87226-87-7; **4**, 87226-88-8; **5**, 87226-89-9; **6**, 87226-90-2; (*E*)-**7**, 87226-91-3; (*Z*)-**7**, 87226-93-5; **8**, 87226-92-4; **9**, 74252-09-8; **10**, 87249-28-3; **11**, 87249-29-4; **12**, 87261-29-8; **13**, 87249-31-8; **14**, 87249-32-9; **15**, 87249-34-1; $Mn(CO)_5Br$, 14516-54-2; $Re(CO)_5Br$, 14220-21-4; $Mn_2(CO)_6(CH_3CN)_2(\mu\text{-}Br)_2$, 38433-31-7; 2-cyanophenol, 611-20-1; 1,3-dibromopropane, 109-64-8; 1,4-bromobutane, 110-52-1.

Contribution from the Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England, and the Department of Chemistry, The Open University, Milton Keynes MK7 6AA, England

^{15}N NMR Studies of Nitrosyl (Bent and Linear), Nitro, and Nitrito Ligands in 4-, 5-, and 6-Coordinate Complexes of the Platinum Metals

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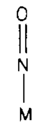
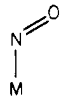
High-field NMR spectroscopy of highly ^{15}N-enriched nitrosyl complexes has shown that nitrogen is deshielded by up to 450 ppm in bent as compared with linear nitrosyl ligands. As in related (e.g., diazenido) groups, the deshielding correlates with the presence of low-energy $n_N \rightarrow \pi^*$ electronic circulations in the magnetic field and so is diagnostic of the bent geometry. Nitrogens in adjacent linear nitrosyl groups are deshielded by 100–150 ppm compared with corresponding mononitrosyl complexes, which may imply substantial overlap of the π HOMOs in the dinitrosyls. There are indications also of some deshielding when nitro and bent nitrosyl groups are adjacent. The 5-coordinate ruthenium dinitrosyl complex $[RuCl(^{15}NO)(NO)(PPh_3)_2]^+$ has been shown by ^{15}N and ^{31}P NMR spectroscopy to have a constitution in solution different from that of the solid. Earlier X-ray crystallographic work gave the structure as square pyramidal with a bent apical nitrosyl ligand and a linear equatorial nitrosyl ligand. The solution contains isomeric structures in equilibrium. However, 5-coordinate rhodium complexes with only one nitrosyl group and no other "ambiguous" ligand, namely $[RhCl(CO)(^{15}NO)(P\text{-}i\text{-}Pr_3)_2]^+$ and $[RhCl(^{15}NO)(^{15}NO_2)(PR_3)_2]$ with R = *i*-Pr, Cy, or Ph, have the square-pyramidal geometry with bent apical nitrosyl in solution as in the solid state. The nitro ligand resonances are found at medium field, between those of nitrite ion and nitroalkanes, as also are those of linear nitrosyls, close to that of free NO^+. Bent nitrosyls, however, resonate at very low field, in the same region as nitrosoalkanes, in which nitrogen carries a lone pair. Nitrogen NMR spectroscopy is thus a useful probe of geometry of nitrosyl ligands and of complexes in solution when alternative structures are available, as through an intramolecular redox process.

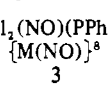
The ability of nitric oxide to coordinate to transition metals in linear (**1**) or bent (**2**) fashion was first established unambiguously as a result of X-ray crystallographic studies in the solid state, particularly by Ibers and co-workers.[1] These studies also suggested that for five-coordinate nitrosyl complexes the potential energy surface connecting alternative linear and bent nitrosyl conformations might be soft, since even for isoelectronic molecules the three limiting geometries illustrated in **3**–**5** were observed in the solid state.[2-5] (In order to limit the confusion that can arise from the NO^+–NO^- formalism, we follow Enemark and Feltham's suggested notation $\{M(NO)\}^x$ to designate nitrosyl complexes.[6]) Further, MNO angles between 120 and 180° are well documented (though less common), notably in complexes with two cis nitrosyl groups.[6] The occurrence of such a soft potential energy surface has been used to account for differences in the substitution and catalytic reactions of metal nitrosyl complexes compared to carbonyl complexes.[7] In addition, the theoretical aspects of nitrosyl binding have been discussed by several workers.[8]



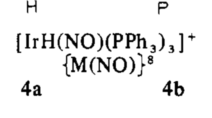
(M-N-O ~ 180°)
1



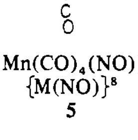
(M-N-O ~ 120°)
2



$[IrCl_2(NO)(PPh_3)_2]$
$\{M(NO)\}^8$
3



$[IrH(NO)(PPh_3)_3]^+$
$\{M(NO)\}^8$
4a **4b**



$[Mn(CO)_4(NO)]$
$\{M(NO)\}^8$
5

In this paper we report the first observations in ^{15}N nuclear magnetic resonance of bent as well as linear nitrosyl ligands in transition-metal complexes, the large difference in nitrogen shifts in the bent compared to the linear ligand showing the value of nitrogen NMR in the structural characterization of nitrosyl complexes in solution. In addition, we have identified ranges of ^{15}N resonances for nitro and hyponitrito ligands

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