# Formation and Molecular Structure of a Dimeric Manganese Isocyanophosphane Complex: $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$

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The reaction of $[(Me_3Si)_2N](Ph)PCl$ with $NaCpMn(CO)_2(CN)$ in THF results in the formation of an isocyanophosphane complex, $CpMn(CO)_2[CNP(Ph)N(SiMe_3)_2]$ (1). Upon standing, 1 slowly evolves CO, and the resulting coordinatively unsaturated fragment dimerizes by coordination of the phosphorus atom on one fragment to the manganese atom of a second fragment. The dimer, $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$, has been partially characterized by spectroscopic techniques and the molecular structure determined by single-crystal X-ray diffraction analysis. The crystals were found to be triclinic of space group $P\bar{1}$ (No. 2) with $a = 9.460$ (4) Å, $b = 10.981$ (5) Å, $c = 11.500$ (5) Å, $\alpha = 87.92$ (4)°, $\beta = 80.93$ (3)°, $\gamma = 71.28$ (3)° with $Z = 1$, $V = 1117.1$ (8) Å$^3$, and $\rho = 1.315$ g cm$^{-3}$. The structure was refined to $R_F = 4.3\%$ and $R_{wF} = 3.7\%$ on 3770 reflections with $F \geq 5\sigma(F)$. The manganese atom has a pseudooctahedral piano-stool geometry, and the phosphorus atom has a distorted tetrahedral geometry. Several important bond distances include Mn–P = 2.200 (1) Å, Mn–C(N) = 1.789 (2) Å, Mn–C(O) = 1.770 (3) Å, P–N(C) = 1.724 (2) Å, $P{-}N(Si)_2$ = 1.705 Å, and C–N = 1.202 (3) Å.

## Introduction

A number of anionic organometalates, $[CpMn(CO)_2(CN)^-]$,[1-3] $[CpMn(CO)(NO)(CN)^-]$,[2] $[CpCo(CN)_3^-]$,[4] $[CpM(CO)(NO)(CN)^-]$ (M = Cr, Mo, W),[2] $[CpFe(CO)(CN)_2^-]$,[5] $[M(CO)_5(CN)^-]$ (M = Cr, Mo, W),[6] $[Mn(CO)_3(NO)(CN)^-]$,[7] and $[Mn_2(CO)_9(CN)^-]$,[8] containing terminal cyanide ligands have been observed to undergo addition reactions at the nitrogen atom by protons, alkyl cations, and group IV (14[34]) organohalides, $R_3MCl$ (M = Si, Ge, and Sn), with the subsequent formation of terminal isonitrile products, $M'{-}C{\equiv}NX$ (X = H, R, $R_3M$). In a few instances, group V (15[34]) organohalides, $R_2MCl$ (M = P, As), have also been observed to form terminal isonitrile addition products, $M'{-}C{\equiv}NPR_2$.[1,2,8] The last observation is made particularly interesting since there are now a number of examples of reactions of halophosphanes with metal carbonylates that result in the formation of terminal, planar metallophosphenium complexes or terminal, pyramidal metallophosphanes[9-14] in which the bicoordinate phosphorus fragment is directly bonded to the metal center. At this time, there are no examples of halophosphane addition to the oxygen atom of a terminal carbonyl in which an isocarbonyl phosphane species is arrested.

The reactivity of metallophosphenium and metallophosphane complexes is expected to be richly variable,[15,16] and selected aspects of the reaction chemistry are under study.[10,12,14,16,17] Interest in this chemistry has led us to explore variations in reactivity as a function of ancillary ligands introduced on the metal center, and in support of these studies, we have investigated reactions of several phosphanes with organocyanometalates. We report here the formation of a new (isocyanophosphane)manganese complex, $CpMn(CO)_2[CNP(Ph)N(SiMe_3)_2]$ (1), and a novel self-condensation product, $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$ (2).[18]

## Experimental Section

**General Information.** Standard vacuum line and inert-atmosphere synthetic techniques were employed in the handling of all reagents and reaction products. Infrared spectra were recorded on a Nicolet Model 6000 FTIR spectrometer from so-

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(18) Abbreviations used in the text include the following: Cp = cyclopentadienide ($C_5H_5^-$), Me = $CH_3$, Et = $C_2H_5$, EtO = $C_2H_5O$, Ph = $C_6H_5$, THF = tetrahydrofuran.

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**Table I. Experimental Data for the X-ray Diffraction Study of $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$**

(A) Crystal Parameters at 20 °C

cryst system: triclinic
space group: $P\bar{1}$
$a = 9.460$ (4) Å
$b = 10.981$ (5) Å
$c = 11.500$ (5) Å
$\alpha = 87.92$ (4)°
$\beta = 80.93$ (3)°
$\gamma = 71.28$ (3)°
$V = 1117.1$ (8) Å$^3$
$Z = 1$
formula: $[MnPSi_2ON_2C_{19}H_{28}]_2$
mol wt = 442.5
$\rho$(calcd) = 1.32 g cm$^{-3}$
$F(000) = 464$
$\mu$(Mo K$\alpha$) = 7.53 cm$^{-1}$

(b) Measurement of Intensity Data

diffractometer: Syntex P3/F
radiation: Mo K$\alpha$ ($\lambda$ = 0.710 69 Å)
monochromator: highly oriented graphite crystal
reflctns measd: $\pm h, \pm k, \pm l$
$2\theta$ range: 1–60°
scan speed: 4–30° min$^{-1}$
scan range: $[2\theta(K\alpha_1) - 1.2°]$ to $[2\theta(K\alpha_2) + 1.2°]$
bdgd measmt: stationary crystal, stationary counter; at the beginning and end of $2\theta$ scan—each for half the time taken for $2\theta$ scan
std reflctns: 3 measd every 141 reflctns [$\bar{3}$00, 040, 006]
reflctns collctd: 13 410 total, yielding 6566 independent reflctns
reflctns obsd: 3770 ($F \geq 5\sigma(F)$)

**Table II. Positional Parameters and Their Estimated Standard Deviations $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$**

| atom | x/a | y/b | z/c |
|---|---|---|---|
| Mn | 0.83472 (4) | 0.24009 (3) | 0.46150 (4) |
| P | 0.86863 (7) | 0.15541 (6) | 0.63534 (6) |
| Si(1) | 1.06728 (9) | 0.21000 (8) | 0.79368 (8) |
| Si(2) | 0.72602 (9) | 0.36029 (8) | 0.82284 (8) |
| N(1) | 0.88646 (21) | 0.24009 (19) | 0.75045 (18) |
| C(1) | 0.63993 (31) | 0.25851 (26) | 0.47522 (27) |
| O(1) | 0.51301 (24) | 0.27782 (23) | 0.47783 (23) |
| C(2) | 0.90631 (24) | 0.07749 (22) | 0.40762 (21) |
| N(2) | 0.96327 (21) | −0.03126 (18) | 0.37099 (18) |
| C(3) | 1.21693 (32) | 0.21426 (32) | 0.67040 (31) |
| C(4) | 1.06514 (46) | 0.33849 (47) | 0.89630 (42) |
| C(5) | 1.12517 (38) | 0.05560 (37) | 0.87350 (31) |
| C(6) | 0.73902 (48) | 0.52555 (31) | 0.79858 (40) |
| C(7) | 0.70115 (43) | 0.32825 (37) | 0.98429 (30) |
| C(8) | 0.54838 (34) | 0.36307 (37) | 0.77059 (36) |
| C(11) | 0.66708 (30) | 0.01376 (26) | 0.63375 (26) |
| C(12) | 0.58332 (33) | −0.06295 (29) | 0.68183 (31) |
| C(13) | 0.57787 (34) | −0.09448 (31) | 0.79826 (33) |
| C(14) | 0.65816 (36) | −0.04996 (34) | 0.86753 (31) |
| C(15) | 0.74239 (31) | 0.02694 (29) | 0.81932 (26) |
| C(16) | 0.74790 (25) | 0.06089 (22) | 0.70183 (23) |
| C(21) | 0.92693 (41) | 0.38912 (31) | 0.48731 (32) |
| C(22) | 1.02975 (37) | 0.29869 (31) | 0.40670 (37) |
| C(23) | 0.95794 (50) | 0.29776 (33) | 0.31014 (34) |
| C(24) | 0.81348 (47) | 0.38470 (36) | 0.33043 (38) |
| C(25) | 0.79351 (39) | 0.44171 (27) | 0.44038 (40) |

lutions contained in a sealed NaCl solution cell. The NMR spectra were recorded on Varian FT-80A and GE NT-360 spectrometers from samples contained in 5-mm tubes. Internal deuterium lock solvents were employed, and the spectra were referenced (external) with $Me_4Si$ ($^1H$, $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). $NaMnCp(CO)_2(CN)$[1,2] and $[(Me_3Si)_2N](Ph)PCl$[19] were prepared by literature methods. Solvents were dried over appropriate drying agents and freshly distilled under dry nitrogen. All solvent transfers were accomplished under vacuum transfer conditions.

**Preparation of $CpMn(CO)_2[CNP(Ph)N(SiMe_3)_2]$ (1).** A solution containing 1.0 g (4.4 mmol) of $NaMnCp(CO)_2(CN)$ in 50 mL of dry THF was prepared in a 100-mL Schlenk flask having a septum-capped side arm. The yellow solution was cooled to −78 °C, and 1.35 g (4.4 mmol) of $[(Me_3Si)_2N](Ph)PCl$ was added with a syringe to the cold THF solution. The mixture was slowly warmed to room temperature and then stirred for 12 h. The reaction mixture (yellow brown solution and white precipitate) was filtered and the solvent evaporated from the filtrate. The resulting oil was extracted with 50 mL of dry benzene and filtered to remove additional NaCl and a very small amount of unreacted $NaMnCp(CO)_2(CN)$. Evaporation of the benzene from the filtrate left a bright golden yellow viscous oil: yield 95%; infrared spectrum (cm$^{-1}$, cyclohexane) 2015 ($\nu_{CN}$, m), 1926 ($\nu_{CO}$, vs), 1913 ($\nu_{CO}$, vs), 1254 (m), 928 (vs), 880 (vs), 847 (vs). Mass spectrum (70 eV, $m/e$ (relative intensity)): [M$^+$], 470 (10); [M − 2CO], 414 (38); [$C_{12}H_{23}Si_2PN^+$], 268 (100); 146 (37); 73 (14). NMR spectra (27 °C): $^{31}P\{^1H\}$ (THF) $\delta$ 89; $^{13}C\{^1H\}$ ($CH_2Cl_2/CD_2Cl_2$) $\delta$ 143.1 (MnCN, $^2J_{CNP}$ = 18.4 Hz), 129.5–128.5 (m, $C_6H_5$), 82.8 ($C_5H_5$), 3.8 ($CH_3$, $^3J_{CP}$ = 7.8 Hz); $^1H$ ($CH_2Cl_2/CD_2Cl_2$) $\delta$ 7.48–7.41 ($C_6H_5$), 4.74 ($C_5H_5$), 0.31 ($CH_3$). Anal. Calcd for $C_{20}H_{22}MnN_2O_2PSi_2$: C, 51.05; H, 6.00; N, 5.96; P, 6.58; Mn, 11.68. Found: C, 51.91; H, 6.51; N, 5.40; P, 7.07; Mn, 10.10.[20]

**Formation of $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$ (2).** Attempts to grow single crystals of 1 from several solvents were unsuccessful. However, it was noted that concentrated THF solutions of 1 left in room light at 25 °C slowly evolved carbon monoxide and a yellow crystalline solid 2 deposited. Yield: ~25%. Attempts to remove adhering oily residues from 2 were unsuccessful, and analytically pure samples were not isolated. Infrared spectrum (cm$^{-1}$) ($CH_2Cl_2$): 2040 ($\nu_{CN}$, m), 1829 ($\nu_{CO}$, vs). NMR spectrum (27 °C): $^{31}P\{^1H\}$ ($CD_2Cl_2$) $\delta$ 85.

**Collection of X-ray Diffraction Data and Solution of the Structure of $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$ (2).** A small crystal (0.11 × 0.18 × 0.36 mm) was sealed in a glass capillary under nitrogen and was centered on a Syntex P3/F automated diffractometer. Determinations of the crystal class, orientation matrix, and accurate unit cell parameters were performed in a standard manner,[21] and diffraction data were collected by using the conditions outlined in Table I.

Examination of the standard reflections during the data collection showed some signs of crystal decay, and the data were scaled on the standards to compensate for the almost 10% decay. The data were corrected for Lorentz and polarization effects and redundant data averaged (agreement, $R$ = 1.7%). An empirical absorption correction based on azimuthal scans was applied. The correction improved the agreement of the azimuthal scan data from 2.10% to 2.04%. The estimated maximum and minimum transmission factors were 0.82 and 0.80, respectively.

The structure was solved by direct methods[22] in the space group $P\bar{1}$, and the reasonable refinement substantiates the space group choice. Direct methods provided the positions of the $MnPN(Si)_2$ fragment. Phasing on this fragment provided the positions of the remaining non-hydrogen atoms. Isotropic refinement[23] on the non-hydrogen atoms converged with $R$ = 12%, and anisotropic refinement on these atoms gave $R$ = 5.4%. The hydrogen atoms were included in idealized positions, riding on their parent atoms and given fixed isotropic $U$'s equal to 1.2 times the last $U_{equiv}$ of their parent atoms. The resulting agreement factors[23] were $R_F$ = 4.3% and $R_{wF}$ = 3.7%. The model was tested for correctness of the position of the cyano group. Interchanging the C≡O and C≡N groups increased the anisotropic agreement factor $R$ from 5.4% to 5.6%. A final difference Fourier synthesis showed no unusual features with no peak greater than 0.37 e Å$^{-3}$. Tables of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters are

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[19] The phosphane was prepared from $PhPCl_2$ and $NaN(SiMe_3)_2$ in $Et_2O$ by a procedure similar to that described for related phosphanes: Zeiss, W.; Feldt, C.; Weis, J.; Dunkel, G. *Chem. Ber.* **1978**, *111*, 1180.

[20] Elemental analyses for 1 were compromised by small amounts of solvent which were retained in the oily product.

[21] Programs used for centering reflections, autoindexing, refinement of cell parameters, and axial photographs are those described in: *Nicolet P3/R3 Operations Manual*; Sparks, R. A., Ed.; Syntex Analytical Instruments: Cupertino, CA, 1978.

[22] The SHELXTL package of programs for calculations and plots is described in: Sheldrick, G. M. *SHELXTL Users Manual, Revision 3*; July 1981, Nicolet XRD Corp. SHELXTL uses scattering factors and anomalous dispersion terms taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1968: Vol. IV.

[23] The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. Discrepancy indices are defined as follows: $R_F = [\sum||F_o| - |F_c||]/\sum|F_o|$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2(F) + |g|F^2]$, $g$ = 0.00011, and the goodness of fit GOF = $[w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables. In this case, GOF = 1.416.

available. Non-hydrogen atom positional parameters are presented in Table II.

## Results and Discussion

The combination of $NaCpMn(CO)_2(CN)$ and $[(Me_3Si)_2N](Ph)PCl$ in a 1:1 ratio in THF results in the formation of a yellow oil identified by elemental analysis and mass, infrared, and NMR spectroscopy as $CpMn(CO)_2[CNP(Ph)N(SiMe_3)_2]$ (1). Carbon monoxide is not evolved during the reaction, and 1 is isolated in good yield. The mass spectrum of 1 displays a parent ion and fragmentation pattern consistent with the proposed formulation of the compound. An infrared spectrum of 1 recorded from a cyclohexane solution in the region 2100–1800 $cm^{-1}$ shows three absorptions at 2015, 1926, and 1913 $cm^{-1}$, assigned to $\nu_{CN}$, $\nu_{CO}(A')$ and $\nu_{CO}(A'')$, respectively. The band pattern is very similar to the $CH_2Cl_2$ solution spectrum reported for $CpMn(CO)_2(CNPPh_2)$,[2] 2020, 1922, and 1904 $cm^{-1}$. Further, $\nu_{CN}$ for 1 is displaced to lower frequency from $\nu_{CN}$ in the salt $NaCpMn(CO)_2(CN)$[1], $\nu_{CN}$ = 2055 $cm^{-1}$, and it is similar to $\nu_{CN}$ in other isocyanophosphane complexes, $CpMn(CO)_2(CNPR_2)$[1]: R = Et, 2024 $cm^{-1}$; R = EtO, 2014 $cm^{-1}$. This displacement of $\nu_{CN}$ upon coordination of the anionic cyanometalate by $PX_2$ units is opposite in direction to the trend observed with $BX_2$ fragments. For example, the coordination of cyanide nitrogen sites displays an up-frequency shift in the following series:[24] $KCpFe(CO)(CN)_2$, 2095 $cm^{-1}$, $CpFe(CO)(CN)(CNBF_2)$, 2175 $cm^{-1}$, $CpFe(CO)(CN)(CNBBr_2)$, 2165 $cm^{-1}$, and $CpFe(CO)(CN)(CNBPh_2)$, 2175 $cm^{-1}$. These differences are expected on the basis of the anticipated differences in electronic demands exerted by $PX_2$ and $BX_2$ fragments.

The $^{31}P\{^1H\}$ NMR spectrum of 1 shows a singlet at $\delta$ 89 shifted significantly upfield of the resonance for the free ligand, $\delta$ 143, and outside of the low-field shift region normally associated with metallophosphenium and metallophosphane compounds.[10–17,25] The shift from the free ligand,[26] $\Delta = -54$, is similar to those displayed by other isocyanophosphane complexes:[1] $CpMn(CO)_2(CNPPh_2)$, $\Delta = -32.4$; $CpMn(CO)_2(CNPEt_2)$, $\Delta = -44$; $CpMn(CO)_2[CNP(OEt)_2]$, $\Delta = -54.8$. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet centered at $\delta$ 143.1 ($^2J_{CP}$ = 18.4 Hz). This resonance falls within a wide range of shifts, $\delta$ 175–105, in organometallic isonitrile compounds,[27] and it is assigned to the cyanide carbon atom of the isocyanophosphane ligand. The corresponding resonance in only one other (isocyanophosphane)manganese complex, $CpMn(CO)_2(CNPPh_2)$, $\delta$ 212.4, has been reported.[2] In this example, P–C coupling was not resolved. Resonances for the phenyl, cyclopentadienyl, and trimethylsilyl groups in 1 were observed in the expected regions of the $^{13}C\{^1H\}$ and $^1H$ NMR spectra.

The analytical and spectroscopic data for 1 outlined above are consistent with data reported previously for related metalloisocyanophosphanes.[1,2] Nonetheless, the contrast in the products formed and reaction paths followed by combinations of metal carbonylates or metal cyanocarbonylates with halophosphanes led us to attempt to obtain single crystals for X-ray diffraction analysis of the unique Mn—C≡N—P structural unit in 1. Crystals, in fact, were obtained slowly from THF solutions of 1 held at 25 °C in room light; however, infrared and $^{31}P$ NMR spectroscopic data indicated the formation of a second product, 2. Unfortunately, the conversion 1 → 2 did not go to completion under these conditions or in boiling cyclohexane or under UV photolysis of cyclohexane solutions of 1. It also proved difficult to separate the crystals of 2 from the oil of 1, and reliable elemental analyses of 2 were not obtained. Infrared spectra[28] of 2 in $CH_2Cl_2$ displayed a single carbonyl band, $\nu_{CO}$ = 1829 $cm^{-1}$, and one cyanide stretch, $\nu_{CN}$ = 2040 $cm^{-1}$. The significant decrease in the carbonyl stretching frequency is consistent with enhanced Mn → CO $\pi$ back-bonding in 2. The $^{31}P\{^1H\}$ NMR spectrum of 2 showed a singlet $\delta$ 85 shifted only slightly upfield from the resonance in 1. $^1H$ and $^{13}C\{^1H\}$ NMR spectra of 2 appeared to be essentially identical with those of 1.

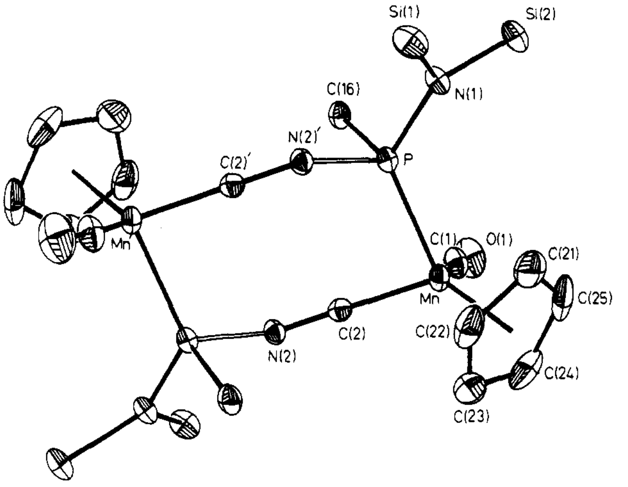

Figure 1. Molecular geometry and atom-labeling scheme for $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$ (25% probability ellipsoids) with the trimethylsilyl methyl groups omitted for clarity.

**Table III. Selected Bond Distances (Å) and Their Estimated Standard Deviations for $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$**

| | | | |
|---|---|---|---|
| Mn–P | 2.200 (1) | Mn–C(1) | 1.770 (3) |
| Mn–C(2) | 1.789 (2) | Mn–C(21) | 2.136 (4) |
| Mn–C(22) | 2.140 (4) | Mn–C(23) | 2.132 (4) |
| Mn–C(24) | 2.133 (4) | Mn–C(25) | 2.133 (3) |
| P–N(1) | 1.705 (2) | P–C(16) | 1.842 (3) |
| P–N(2) | 1.724 (2) | Si(1)–N(1) | 1.782 (2) |
| C(2)–N(2) | 1.202 (3) | Si(2)–N(1) | 1.770 (2) |
| | | C(1)–O(1) | 1.146 (4) |

**Table IV. Selected Bond Angles (°) and Their Estimated Standard Deviations for $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2$**

| | | | |
|---|---|---|---|
| P–Mn–C(1) | 96.7 (1) | P–Mn–C(2) | 85.2 (1) |
| C(1)–Mn–C(2) | 97.7 (1) | Mn–P–C(16) | 118.6 (1) |
| Mn(1)–P–N(1) | 122.7 (1) | Mn–P–N(2) | 112.0 (1) |
| N(1)–P–C(16) | 104.5 (1) | C(16)–P–N(2) | 95.7 (1) |
| N(1)–P–N(2) | 98.5 (1) | P–N(1)–Si(2) | 119.6 (1) |
| P–N(1)–Si(1) | 119.7 (1) | Mn–C(1)–O(1) | 174.7 (3) |
| Si(1)–N(1)Si(2) | 120.8 (1) | C(2)–N(2)–P | 139.8 (2) |
| Mn–C(2)–N(2) | 175.9 (2) | | |

The molecular structure determination for 2 revealed an unexpected and interesting chemical event in the conversion of 1 to 2. A view of the molecule is shown in Figure 1, and important bond distances and angles are presented in Tables III and IV. Compound 2 is a dimer of $\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}$ with a nonplanar eight-membered $\overline{\text{Mn-C-N-P-Mn-C-N-P}}$ ring which displays $C_i$ symmetry. Each Mn atom has a three-legged

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[28] The infrared spectra of 2 are very sensitive to the solvent: $\nu_{CO}$(THF) 1861 $cm^{-1}$; $\nu_{CO}$(cyclohexane) 1870 $cm^{-1}$; $\nu_{CO}$(KBr) 1816 $cm^{-1}$. The cyanide stretch was detected only from the $CH_2Cl_2$ solutions.

piano-stool structure that can be compared with the structures of the mononuclear isocyanide compound[29] $CpMn(CO)_2(CN\text{-}t\text{-}Bu)$ (**3**) and several $CpMn(CO)_2L$ compounds (L = CO, $PPh_3$, $PPh_2H$).[30] The single terminal Mn–CO distance, 1.770 (3) Å, falls within the range of distances, 1.75–1.78 Å, found in the $CpMn(CO)_2L$ compounds,[29,30] and the average ($Mn-C_{Cp}$) distance, 2.135 Å, is comparable with the related averages in the $CpMn(CO)_2L$ compounds.[29,30] The tripod substituent angles P–Mn–C(2) = 85.2 (1)°, P–Mn–C(1) = 96.7 (1)°, and C(1)–Mn–C(2) = 97.7 (1)° show a greater variation than typically found in the $CpMn(CO)_2L$ complexes (90°–94°), and the confining nature of the internal ring structure is most likely responsible for this feature. The Mn—CN distance, 1.789 (2) Å, in **2** is shorter than the Mn—CN distance, 1.85 (2) Å, in **3** while the C═N distance, 1.202 (3) Å, in **2** is longer than the C═N distance, 1.17 (2) Å, in **3** although in the latter case the difference may not be statistically significant. Nonetheless, the trends in bond distances are consistent with the differing electronic demands of the respective isonitrile substituents, $P(Ph)[N(SiMe_3)_2](Mn')$ and *t*-Bu. The Mn–C(2)–N(2) angle in **2** is nearly linear, 175.9 (2)°, and this feature is similar to that found in **3**, 177 (2)°. However, the angle C(2)–N(2)–P′, 139.8 (2)°, is more severely bent than its counterpart angle $C-N-C(CH_3)_3$, 172 (2)° in **3**.

The geometry at the phosphorus atoms is pseudotetrahedral with the angles about phosphorus falling in the range 95.7–122.7°. The Mn–P bond distance 2.200 (1) Å is the same as that found in $CpMn(CO)_2[P(Ph)_2(H)]$,[30c] 2.201 (4) Å, but these are shorter than the typical range of distances, 2.25–2.40 Å, found in a variety of neutral organomanganese phosphane complexes.[30,31] The short distance indicates that the isocyanophosphane acts as a particularly good ligand toward the CpMn(CO) fragment. The P–N(1) bond distance, 1.705 (2) Å, is essentially the same as the related $P-N(SiMe_3)_2$ distance in the planar metallophosphenium compound $CpMo(CO)_2[P(Ph)N(SiMe_3)_2]$, 1.698 (2) Å, in which the phosphorus lone pair is involved in the Mo–P bond, and in the pseudotetrahedral borane complex $CpMo(CO)_2[P(\mu\text{-}BH_3)(Ph)N(SiMe_3)_2]$,[17] 1.700 (3) Å, in which the phosphorus lone pair is donated to the borane group. The P–N(1) distance in **2** also compares favorably with the distances in $[(OC)_5Cr](Me_3Si)_2NP-Cr(CO)_4-PN(SiMe_3)_2[Cr(CO)_5]$,[33] 1.708 (5) Å, and in $(Me_3Si)_2NP[Cr(CO)_5]_2$,[33] 1.697 (3) Å. The P–N(2) distance involving the original cyanide ligand is somewhat longer, 1.724 (2) Å; however, this distance is shorter than the $P-N(SiMe_3)_2$ distance, 1.734 (4) Å, found in the pyramidal metallophosphane compound $CpFe(CO)_2[P(Ph)N(SiMe_3)_2]$.[32] The remaining bond distances and angles in the isocyanophosphane ligand unit show no unusual deviations.

The chemistry, spectroscopic data, and molecular structure determination are consistent with Scheme I shown here. The formation of the isocyanophosphane complex **1** is consistent with the chemistry reported previously by Höfler[1] and Behrens;[2] however, there is no precedent for th subsequent dimerization of **1** with loss of carbon monoxide. Höfler, however, noticed that $CpMn(CO)_2CNPPh_2$ and $CpMn(CO)_2THF$ combined to give a bimetallic complex, $[CpMn(CO)_2]_2(CNPPh_2)$. The conversion of **1** to **2** suggests that **1** may display some additional novel reactivity and some chemistry of the compound is under examination.

**Scheme I**

$$NaCpMn(CO)_2CN + [(Me_3Si)_2N](Ph)PCl \xrightarrow[-NaCl]{THF} \underset{1}{CpMn(CO)_2[CNP(Ph)N(SiMe_3)_2]} \xrightarrow{-CO} \underset{2}{\{CpMn(CO)[CNP(Ph)N(SiMe_3)_2]\}_2}$$

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**Registry No.** 1, 111410-21-0; 2, 111435-19-9; $NaMnCp(CO)_2(CN)$, 12317-62-3; $[(Me_3Si)_2N](Ph)PCl$, 84174-75-4.

**Supplementary Material Available:** Listings of anisotropic thermal parameters, hydrogen atom positional parameters, and bond distances and angles (5 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current mast head page.

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[34] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13-18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)