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Poly(tertiary phosphines and arsines). 20.[1] Some Reactions of (Methylamino)bis(dimethoxyphosphine) and Crystal Structure of (μ-Carbonyl)[μ-(methylamino)bis(dimethoxyphosphine)]bis(tricarbonyliron), $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$

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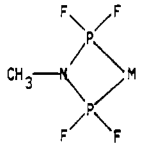
Reactions of the complexes (norbornadiene)M(CO)$_4$ (M = Cr and Mo) with $CH_3N[P(OCH_3)_2]_2$ give the corresponding $CH_3N[P(OCH_3)_2]_2M(CO)_4$ chelate complexes. Reactions of iron carbonyls with $CH_3N[P(OCH_3)_2]_2$ under appropriate conditions give the bridged binuclear complexes $\{CH_3N[P(OCH_3)_2]_2\}_nFe_2(CO)_{9-2n}$ (n = 1 and 2). The infrared ν(CO) frequencies of metal carbonyl complexes of $CH_3N[P(OCH_3)_2]_2$ are consistently lower than those of analogous $CH_3N(PF_2)_2$ complexes, in accord with the lower π-acceptor strength of $CH_3N[P(OCH_3)_2]_2$ relative to that of $CH_3N(PF_2)_2$. Single-crystal X-ray diffraction analysis shows the complex $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) to have an Fe-Fe bond 2.6606 (5) Å long that is bridged by one CO group and by the bidentate ligand $CH_3N[P(OCH_3)_2]_2$. The CO group, the N atom, and the midpoint of the Fe-Fe bond are located on a crystallographic mirror plane. The Fe-P bond length is 2.1919 (5) Å, and the P-N bond length is 1.665 (1) Å. The Fe_2P_2N ring conformation is almost exactly plane, unusual for either M_2P_2N or M_2P_2C rings. The Fe_2P_2N best plane is at ~90° to the best plane through the two Fe atoms and five of the carbonyl carbon atoms, including the bridging carbon. Except for the nearly plane Fe_2P_2N ring, the structure of the moiety $Fe_2P_2N(CO)_7$ in **3** is remarkably close, even in some rather fine details, to that of the moiety $Fe_2P_2C(CO)_7$ in $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**) as described by Cotton and Troup.

Introduction

During the past several years the transition-metal coordination chemistry of the small-bite bidentate fluorophosphine $CH_3N(PF_2)_2$ has been studied extensively at the University of Georgia.[3] This work had led to the preparation of a variety of metal chelates of two types: mononuclear derivatives containing four-membered chelate rings (**1**) and binuclear derivatives containing five-membered chelate rings (**2**). These results make of interest the transition-metal coordination chemistry of other substituted phosphines of the type $RN(PX_2)_2$. In this connection we have been studying the coordination chemistry of $CH_3N[P(OCH_3)_2]_2$ in order to ascertain the effects of substituting the fluorine atoms in $CH_3N(PF_2)_2$ with the less electronegative methoxy groups. A previous paper in this series[4] discusses the binuclear cobalt complex $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$; this complex is of particular interest since one cobalt atom exhibits approximate trigonal-bipyramidal coordination and the other cobalt atom exhibits approximate square-pyramidal coordination despite the fact that each cobalt atom has the same ligand set. This paper describes some $CH_3N[P(OCH_3)_2]_2$ complexes of other metal carbonyls. Because some of the iron carbonyl chemistry of this ligand was initially obscure, we determined the structure of one of the iron carbonyl complexes by X-ray crystal-structure analysis; this complex turned out to be $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**), closely related to the complex $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**), whose structure has also been determined by X-ray analysis.[5]



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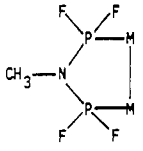

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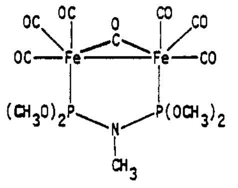

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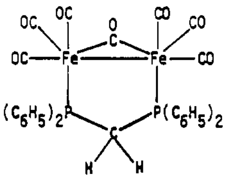

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Experimental Section

General aspects of the experimental and spectroscopic techniques were similar to those used in previous work from the University of Georgia.[4,6] Phosphorus-31 NMR chemical shifts are reported in ppm downfield from external 85% H_3PO_4. Infrared spectra in the ν(CO) region of the new $CH_3N[P(OCH_3)_2]_2$ complexes and their $CH_3N(PF_2)_2$ analogues[6,7] are listed in Table I.

The ligand $CH_3N[P(OCH_3)_2]_2$ was prepared by the procedure described in a previous paper of this series.[4]

Preparation of $CH_3N[P(OCH_3)_2]_2Cr(CO)_4$. A mixture of 0.78 g (3.1 mmol) of (norbornadiene)tetracarbonylchromium,[8] 0.66 g (3.1 mmol) of $CH_3N[P(OCH_3)_2]_2$, and 200 mL of methylcyclohexane was boiled under reflux until the original yellow color disappeared (2.0 h). Evaporation of the solvent at 40 °C (25 mm) followed by sublimation of the residue at 80 °C (0.1 mm) gave 1.16 g (~100% yield) of white crystalline $CH_3N[P(OCH_3)_2]_2Cr(CO)_4$, mp 132-133 °C. Proton NMR spectrum ($CDCl_3$): δ 3.66 (doublet, 13-Hz separation, OCH_3) and 2.53 (broad triplet, 7-Hz separation, NCH_3). Phosphorus-31 NMR spectrum (CH_2Cl_2): δ 165.3. Anal. Calcd for $C_9H_{15}CrNO_8P_2$: C, 28.5; H, 4.0; N, 3.7. Found: C, 28.3; H, 4.0; N, 3.6.

Preparation of $CH_3N[P(OCH_3)_2]_2Mo(CO)_4$. A mixture of 1.0 g (3.3 mmol) of (norbornadiene)tetracarbonylmolybdenum,[8] 0.72 g (3.3 mmol) of $CH_3N[P(OCH_3)_2]_2$, and 200 mL of hexane was boiled under reflux for 1 day. Evaporation of the solvent followed by sublimation of the residue at 80 °C (0.05 mm) gave 1.40 g (~100% yield) of white crystalline $CH_3N[P(OCH_3)_2]_2Mo(CO)_4$, mp 140-141 °C. Proton NMR spectrum ($CDCl_3$): δ 3.61 (triplet, 7-Hz separation, OCH_3) and 2.49 (triplet, 9-Hz separation, NCH_3). Phosphorus-31 NMR spectrum (CH_2Cl_2): δ 148.4. Mass spectrum (200 °C probe, relative intensities in parentheses): $CH_3N[P(OCH_3)_2]_2Mo(CO)_4^+$ (56), $CH_3N[P(OCH_3)_2]_2Mo(CO)_3^+$ (33), $CH_3N[P(OCH_3)_2]_2Mo(CO)_2^+$ (56), $CH_3N[P(OCH_3)_2]_2MoCO^+$ (69), $CH_3N[P(OCH_3)_2]_2Mo^+$

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(1) For part 19 of this series see: King, R. B.; Bibber, J. W. *Inorg. Chim. Acta* **1982**, *59*, 197.

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Table I. Comparison of ν(CO) Frequencies in the Infrared Spectra of Analogous Metal Carbonyl Complexes of $CH_3N(PX_2)$ (X = F and OCH_3)

		carbonyl frequencies, cm^{-1}					
		terminal CO					
compd	medium						μ-CO
$CH_3N(PX_2)_2Cr(CO)_4$							
X = F	hexane	2053	1992	1980	1967		
X = OCH_3	CH_2Cl_2	2020	1940	1920	1890		
$CH_3N(PX_2)_2Mo(CO)_4$							
X = F	hexane	2060	1997	1984	1975		
X = OCH_3	CH_2Cl_2	2035	1910	1900	1890		
$CH_3N(PX_2)_2Fe_2(CO)_7$							
X = F	pentane	2090	2040	2025	1995	1982	1805
X = OCH_3	hexane	2050	1995	1977	1962	1950	1766
$[CH_3N(PX_2)_2]_2Fe_2(CO)_5$							
X = F	hexane	2066	2026	1992	1978		1786
X = OCH_3	KBr	1990	1939	1908	1890		1711

(100). Anal. Calcd for $C_9H_{15}MoNO_8P_2$: C, 25.5; H, 3.6; N, 3.3. Found: C, 25.8; H, 3.7; N, 3.3.

Preparation of $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$. A mixture of 5.0 g (13.7 mmol) of $Fe_2(CO)_9$, 1.8 g (8.4 mmol) of $CH_3N[P(OCH_3)_2]_2$, and ~50 mL of hexane was boiled under reflux for 30 min. During this period the $Fe_2(CO)_9$ dissolved to give an orange solution. The reaction mixture was concentrated under vacuum to half of its volume and then cooled to −78 °C. The resulting orange precipitate was repeatedly crystallized from hexane to give ~2.5 g (~60% yield) of $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$, mp 122–124 °C. Proton NMR spectrum ($CDCl_3$): δ 3.70 (triplet, 6-Hz separation, OCH_3) and 2.59 (triplet, 7-Hz separation, NCH_3). Phosphorus NMR spectrum (CH_2Cl_2): δ 170.9. Anal. Calcd for $C_{12}H_{15}Fe_2NO_{11}P_2$: C, 27.6; H, 2.9; N, 2.7. Found: C, 27.5; H, 2.9; N, 2.7.

Preparation of $\{CH_3N[P(OCH_3)_2]_2\}_2Fe_2(CO)_5$. (a) From $Fe(CO)_5$. A mixture of 1.9 g (9.3 mmol) of $Fe(CO)_5$, 2.0 g (9.3 mmol) of $CH_3N[P(OCH_3)_2]_2$, and 150 mL of hexane was exposed to the ultraviolet radiation from an Englehard-Hanovia 450-W lamp for 3 h through a glass filter. Solvent was removed from the resulting orange solution at ~25 °C (25 mm). The residue was crystallized several times from hot hexane to give ~1.6 g (50% yield) of orange $\{CH_3N[P(OCH_3)_2]_2\}_2Fe_2(CO)_5$, identified by comparison of its physical and spectroscopic properties with those of material prepared from $Fe_2(CO)_9$ as described below.

(b) From $Fe_2(CO)_9$. A mixture of 5.0 g (13.7 mmol) of $Fe_2(CO)_9$, 6.0 g (27.9 mmol) of $CH_3N[P(OCH_3)_2]_2$, and 500 mL of hexane was boiled under reflux for 1 h. The $Fe_2(CO)_9$ dissolved after about 20 min of such heating. Removal of solvent (25 °C, 25 mm) from the filtered reaction mixture gave an orange liquid indicated by thin-layer chromatography to be a mixture of at least three components. The infrared spectrum of the liquid in the ν(CO) region showed strong terminal ν(CO) frequencies but no significant bridging ν(CO) frequencies.

In view of the difficulty in separating pure compounds directly from this liquid, a 1.5-g sample of it was heated further with 1.5 g (4.0 mmol) of $Fe_2(CO)_9$ in ~100 mL of hexane for 1 h. Concentration of the reaction mixture to half of its volume followed by cooling in a −78 °C bath gave an orange precipitate. Several recrystallizations of this precipitate from hot hexane gave orange $\{CH_3N[P(OCH_3)_2]_2\}_2Fe_2(CO)_5$, mp 203–205 °C. Proton NMR spectrum ($CDCl_3$): δ 3.71 (quintet, 3-Hz separation, OCH_3) and 2.62 (quintet, 3-Hz separation, NCH_3). Phosphorus-31 NMR spectrum (CH_2Cl_2): δ 178.3. Anal. Calcd for $C_{15}H_{30}Fe_2N_2O_{13}P_4$: C, 26.4; H, 4.4; N, 4.1. Found: C, 26.3; H, 4.4; N, 4.1.

Structure Determination of $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ by X-ray Diffraction. A crystal specimen from dry hexane solution bounded by eight plane faces and having maximum and minimum diameters of about 0.48 and 0.18 mm was selected. Preliminary examination by X-ray precession photography showed the crystal to be monoclinic. The only systematic absences were for reflections $0k0$ for odd k, indicating that the space group is either $P2_1$ or $P2_1/m$. The following unit-cell parameters and estimated standard deviations were derived by the method of least squares from angle data recorded at about 20–22 °C with the Oak Ridge automatic computer-controlled X-ray diffractometer[9] for Mo Kα_1 reflections (wavelength taken as 0.709 30 Å): a = 9.1429 (17) Å, b = 15.9765 (51) Å, c = 6.8758 (13) Å, β = 101.00 (1)°. The experimental density, determined by the "sink-or-float" method, is 1.78 (4) g/cm^3. The calculated density is 1.761 g/cm^3 for the two molecules of $CH_3N[P(OCH_3)_2]Fe_2(CO)_7$ (molecular weight 522.87) per unit cell subsequently found in the structure analysis.

Intensities were recorded by the θ–2θ step-scan technique using niobium-filtered Mo Kα radiation for the reflections of the hkl and $hk\bar{l}$ octants of the limiting sphere defined by a maximum 2θ of 64°. The 2θ step was 0.05°, and the scan width was variable, increasing from an initial 2.0° at low 2θ so as to accommodate the α_1–α_2 splitting. The counting time was 40 s at the initial and final points, which were used to compute background, and 2 s at every other point of each scan. The observations included about 1500 duplicate intensities and periodic observations of three reference reflections.

The data for the reference reflections showed that over the time of the data collection, which extended to about 3 weeks because of instrumental malfunctions, the reflective power of the crystal decreased by about 4.5%. Subsequently when the Lorentz, polarization, and absorption corrections were applied, corrections were also made for this slight deterioration of the crystal. Although the stoichiometry of the compound was not known and the density of the crystal had not been determined at this stage, approximate absorption corrections were computed by the method of Busing and Levy.[10] In measuring the crystal for the absorption calculation, we observed that the external symmetry of the crystal was that of crystal class $2/m$ rather than class 2, as indicated by the fact that the eight crystal faces were identified as those of the forms {001}, {020}, and {110}. This observation fixed the space group as $P2_1/m$ with near certainty.

By averaging the data for the replicate reflections, we derived a set of structure-factor squares F_o^2 and statistical standard errors $\sigma_s(F_o^2)$ for 3560 independent reflections. For later use in least-squares refinement, the standard errors of the observations were adjusted according to the equation

$$\sigma^2(F_o^2) = \sigma_s^2(F_o^2) + (0.03F_o^2)^2 \qquad (1)$$

The term $(0.03F_o^2)^2$ is added to the variance to make some allowance for deficiencies of the model and for instability in the generator and counter circuitry.[11] The intensities were placed on an approximate absolute scale by the least-squares procedure embodied in the program ORESTES,[12] which was also used to apply statistical tests that removed any remaining doubt that the space group is $P2_1/m$.

The structure analysis was started before the analytical data on the compound were available when there were no clues as to its identity except the knowledge of what reactants produced it. From a Patterson map, the cell volume, and the experimental density, we inferred that the unknown complex was probably one with the formula $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ having exact mirror symmetry in the crystal, with both the $CH_3N[P(OCH_3)_2]_2$ group and a carbonyl group bridging the span of an iron–iron bond bisected by the mirror plane. The eight highest peaks of the Patterson map after the origin peak were readily interpreted as Fe–Fe, P–P and Fe–P peaks, so that the starting

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(12) Written by W. E. Thiessen and H. A. Levy of the Oak Ridge National Laboratory.

Table II. Coordinates of the Atoms in the Crystal Structure of $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$, Parameters of the Constrained Refinement[a] Used To Position the Hydrogen Atoms, and Isotropic Thermal Parameters U_{iso}[b] of the Hydrogen Atoms

Positional and Thermal Parameters

atom	x	y	z	U_{iso}, Å^2
Fe	0.10843 (3)	0.16673 (2)	0.06268 (4)	
P	0.33021 (5)	0.15947 (3)	0.25135 (7)	
O(1)	0.22869 (25)	0.25000	−0.25506 (31)	
O(2)	−0.18228 (19)	0.15324 (12)	−0.20283 (28)	
O(3)	0.17173 (19)	0.00660 (11)	−0.10343 (27)	
O(4)	−0.03606 (23)	0.14689 (14)	0.40985 (29)	
O(5)	0.34274 (17)	0.11225 (9)	0.45768 (20)	
O(6)	0.45613 (16)	0.10649 (9)	0.17220 (21)	
N	0.41290 (25)	0.25000	0.32432 (35)	
C(1)	0.17837 (29)	0.25000	−0.11054 (41)	
C(2)	−0.06988 (23)	0.16172 (13)	−0.10048 (33)	
C(3)	0.14870 (23)	0.07041 (14)	−0.03785 (31)	
C(4)	0.02237 (25)	0.15579 (15)	0.28016 (33)	
C(5)	0.29890 (32)	0.02548 (16)	0.46174 (39)	
C(6)	0.50100 (30)	0.12429 (17)	−0.01175 (43)	
C(7)	0.56179 (38)	0.25000	0.45999 (58)	
H(5a)	0.3293	0.0054	0.5861	0.133 (8)
H(5b)	0.1984	0.0222	0.4264	0.133
H(5c)	0.3425	−0.0036	0.3751	0.133
H(6a)	0.5482	0.0788	−0.0488	0.098 (7)
H(6b)	0.4188	0.1360	−0.1040	0.098
H(6c)	0.5634	0.1689	0.0054	0.098
H(7a)	0.5477	0.2500	0.5868	0.105 (10)
H(7b)	0.6122	0.2035	0.4361	0.105

Constrained-Refinement Parameters

C–H = 0.91 (1) Å O–C–H = N–C–H = 108.7 (9)°

H(5a)–C(5)–O(5)–P[c] = 169.1 (1.6)° H(7a)–C(7)–N···C(1)[c] = 180°

H(6a)–C(6)–O(6)–P[c] = −161.4 (1.4)°

[a] See text for explanation. [b] The temperature factors used for the hydrogen atoms have the form $\exp[-8\pi^2 U_{iso}(\sin^2\theta)/\lambda^2]$. [c] Torsion angles.

coordinates for the iron and phosphorus atoms could be deduced. The first Fourier map, with phase signs from a structure-factor calculation including only the iron and phosphorus atoms, yielded the positions of the remainder of the 16 non-hydrogen atoms of the asymmetric unit, which is half of the molecule. Full-matrix least-squares refinement of the coordinates and anisotropic thermal parameters of these 16 atoms proceeded smoothly. At an advanced refinement stage, the absorption calculation was repeated with the value of 16.4 cm^{-1} for the absorption coefficient, calculated for the known content of the unit cell from tabulated mass attenuation coefficients.[13a] At a nearly final stage of refinement approximate positions were found in a difference map for the eight hydrogen atoms of the asymmetric unit. In the subsequent least-squares cycles each methyl group was constrained to have exact C_{3v}-$3m$ symmetry about its C–X axis (X = O or N). The following parameters relating to the hydrogen atoms were adjusted: a single common isotropic thermal parameter for the H atoms of each CH_3 group; a single common length for all eight C–H bonds; a single common angle X–C–H; a torsion angle H–C–O–P to define the orientation of each of the two CH_3 groups attached to oxygen atoms. The orientation of the CH_3 group on the N atom was held fixed, one H atom being on the mirror plane. The scattering factors used, including the anomalous contributions for iron and phosphorus, were from the standard source.[13b] In the final cycles, 2533 F_o^2 values were used, each with a weight of $1/\sigma^2(F_o^2)$. The 985 reflections having $F_o^2 < 2\sigma(F_o^2)$ were given zero weights, as were all 22 reflections having $2\theta < 10.5°$. The latter were rejected because their lower angle backgrounds had clearly not been properly measured because of the filter-edge effect, which resulted characteristically in too high a value for F_o^2. In the final cycle no parameter of the 136 adjusted shifted by as much as 1% of the corresponding estimated standard deviations. On the basis of the 2533 observations included with nonzero weights, the final values of the usual measures of goodness of fit are as follows: $R(F) = 0.036$, $R(F)^2 = 0.042$, $R_w(F^2) = 0.070$, $\sigma_1 = 1.308$.

Table IV. Bond Lengths[a] (Å) in $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) and Corresponding Lengths in the Related Compound $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**)

bond	**3**	**4**	bond	**3**	**4**
Fe–Fe	2.6606 (5)	2.709 (2)[a]	P–N[b]	1.665 (1)	1.845 (10)
Fe–P	2.1919 (5)	2.254 (3)	C(1)–O(1)	1.172 (3)	1.190 (10)[a]
Fe–C(1)	1.972 (2)	1.995 (10)	C(2)–O(2)	1.138 (3)	1.140 (10)
Fe–C(2)	1.796 (2)	1.790 (10)	C(3)–O(3)	1.150 (3)	1.150 (10)
Fe–C(3)	1.755 (2)	1.760 (10)	C(4)–O(4)	1.133 (3)	1.150 (10)
Fe–C(4)	1.826 (2)	1.815 (10)	C(5)–O(5)	1.445 (3)	
P–O(5)	1.592 (1)		C(6)–O(6)	1.431 (3)	
P–O(6)	1.605 (1)		C(7)–N	1.496 (4)	

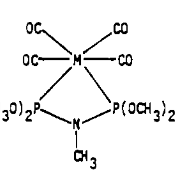
[a] Except for bonds Fe–Fe and C(1)–O(1) the entries for **4** are averages of two chemically equivalent but crystallographically nonequivalent bond lengths. The standard errors are all for individual, unaveraged bond lengths. [b] The corresponding bond in **4** is the P–CH_2 bond.

The final coordinates of all atoms and the parameters used in refinement of the methyl groups are given in Table II. The anisotropic thermal parameters are in Table III (in supplementary material). A listing of observed and calculated structure-factor squares with standard errors is also available as supplementary material.

The standard Oak Ridge National Laboratory crystallographic computer programs were used in this work.[4]

Results and Discussion

Preparative Studies. The reactions used in this work to prepare metal carbonyl complexes of $CH_3N[P(OCH_3)_2]_2$ are similar to those used to prepare analogous metal carbonyl complexes of $CH_3N(PF_2)_2$ and other related ligands. Thus, the reactions of the norbornadiene complexes $C_7H_8M(CO)_4$ (M = Cr and Mo) with $CH_3N[P(OCH_3)_2]_2$ to give $CH_3N[P(OCH_3)_2]_2M(CO)_4$ (**5**, M = Cr and Mo) represent a standard method[16,17] for the preparation of *cis*-$L_2M(CO)_4$ complexes.



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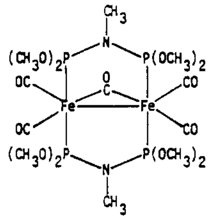

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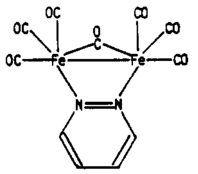

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The reactions of iron carbonyls with $CH_3N[P(OCH_3)_2]_2$ appear to give several products, depending upon the reaction conditions. The reaction of $Fe(CO)_5$ with $CH_3N[P(OCH_3)_2]_2$ does not proceed in boiling hexane in the absence of ultraviolet irradiation. However, ultraviolet irradiation of $Fe(CO)_5$ with $CH_3N[P(OCH_3)_2]_2$ leads to $\{CH_3N[P(OCH_3)_2]_2\}_2Fe_2(CO)_5$ (**6**), in analogy to the formation of $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ by the ultraviolet irradiation of $Fe(CO)_5$ with $CH_3N(PF_2)_2$ in relatively nonpolar solvents such as pentane or diethyl ether.[6]

The reaction of $Fe_2(CO)_9$ with $CH_3N[P(OCH_3)_2]_2$ is more complicated. Thus, reaction of excess $Fe_2(CO)_9$ with $CH_3N[P(OCH_3)_2]_2$ appears to proceed according to eq 2, analogous

$$Fe_2(CO)_9 + CH_3N[P(OCH_3)_2]_2 \rightarrow CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7 + 2CO \quad (2)$$

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Table V. Valence Angles[a] (Deg) in $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) and Corresponding Angles in the Related Compound $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**)

atoms	3	4	atoms	3	4
Fe–Fe–P	93.04 (2)	93.7 (1)	Fe–P–N[b]	116.6 (1)	110.8 (3)
Fe–Fe–C(1)	47.6 (1)	47.2 (3)	Fe–P–O(5)	117.1 (1)	
Fe–Fe–C(2)	92.6 (1)	92.6 (4)	Fe–P–O(6)	118.0 (1)	
Fe–Fe–C(3)	151.3 (1)	154.3 (4)	N–P–O(5)	101.1 (1)	
Fe–Fe–C(4)	95.5 (1)	94.7 (4)	N–P–O(6)	104.3 (1)	
P–Fe–C(1)	91.3 (1)	92.0 (3)	O(5)–P–O(6)	96.8 (1)	
P–Fe–C(2)	174.0 (1)	171.5 (4)	P–N–P[c]	120.7 (1)	109.0 (5)*
P–Fe–C(3)	86.9 (1)	86.5 (3)	P–N–C(7)	119.7 (1)	
P–Fe–C(4)	90.3 (1)	92.0 (4)	Fe–C(1)–O(1)	137.5 (1)	137.1 (9)
C(1)–Fe–C(2)	90.7 (1)	90.1 (1)	Fe–C(1)–Fe	84.9 (1)	85.6 (5)*
C(1)–Fe–C(3)	103.7 (1)	107.5 (5)	Fe–C(2)–O(2)	175.7 (2)	176.6 (1.0)
C(1)–Fe–C(4)	143.1 (1)	141.6 (5)	Fe–C(3)–O(3)	178.4 (2)	177.1 (1.1)
C(2)–Fe–C(3)	87.0 (1)	87.2 (5)	Fe–C(4)–O(4)	176.8 (2)	174.1 (1.2)
C(2)–Fe–C(4)	91.5 (1)	91.0 (6)	P–O(5)–C(5)	119.9 (2)	
C(3)–Fe–C(4)	113.2 (1)	110.9 (5)	P–O(6)–C(6)	122.7 (2)	

[a] Except for the angles marked with an asterisk, the entries for **4** are the averages of two chemically equivalent but crystallographically nonequivalent angles. The standard errors are all for individual, unaveraged angles. [b] The corresponding angle in **4** is Fe–P–CH_2. [c] The corresponding angle in **4** is P–CH_2–P.

to the formation of $CH_3N(PF_2)_2Fe_2(CO)_7$ from $Fe_2(CO)_9$ and $CH_3N(PF_2)_2$[6]. On the other hand, use of an excess of $CH_3N[P(OCH_3)_2]_2$ in the reaction with $Fe_2(CO)_9$ leads to a complex mixture of liquid products that has not been separated into pure compounds. However, under forcing conditions $\{CH_3N[P(OCH_3)_2]_2\}_2Fe_2(CO)_5$ (**6**) can be separated from the $Fe_2(CO)_9/CH_3N[P(OCH_3)_2]_2$ reaction mixture. The reaction of $Fe_2(CO)_9$ with $CH_3N[P(OCH_3)_2]_2$ thus appears to parallel the reported[16] reaction of $Fe_2(CO)_9$ with $(C_2H_5O)_2POP(OC_2H_5)_2$ in which analogues of **3** and **6** are produced in addition to several other products without metal–metal bonds and bridging carbonyl groups.

Spectroscopic Studies. The lower electronegativity of methoxy substitutents makes $CH_3N[P(OCH_3)_2]_2$ a weaker π acceptor than $CH_3N(PF_2)_2$. Therefore, the metal–carbon bond order is higher, the carbon–oxygen bond order is lower, and the $\nu(CO)$ frequencies are lower in metal carbonyl complexes of $CH_3N[P(OCH_3)_2]_2$ than in corresponding metal carbonyl complexes of $CH_3N(PF_2)_2$.[17] Infrared $\nu(CO)$ data showing this effect in the new compounds reported in this paper are shown in Table I.

The proton NMR spectra of the metal carbonyl complexes of $CH_3N[P(OCH_3)_2]_2$ exhibit the expected OCH_3 and NCH_3 resonances having approximately the 4:1 relative areas required by the stoichiometry of the ligand. Strong virtual coupling effects[18,19] make the multiplicities of most of the proton NMR resonances in the $CH_3N[P(OCH_3)_2]_2$ group appropriate for the numbers of phosphorus atoms in the molecules, the major exception being the CH_3O resonance in $CH_3N[P(OCH_3)_2]_2Cr(CO)_4$. Thus, all other proton NMR resonances in the complexes $CH_3N[P(OCH_3)_2]_2M(CO)_4$ (**5**, M = Cr and Co) and those in $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**), each of which contains two phosphorus atoms, are triplets; and both proton NMR resonances in the complex $\{CH_3N[P(OCH_3)_2]_2\}_2Fe_2(CO)_5$ (**6**), which contains four phosphorus atoms, are apparent quintets. The proton NMR spectrum therefore provides a useful indication of the number of $CH_3N[P(OCH_3)_2]_2$ ligands in metal complexes.

Structure of $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$. The $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ molecule (**3**), whose geometry is shown in Figure 1, is closely related in structure to $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**) and to (1,2-diazine)$Fe_2(CO)_7$ (**7**), whose crystal structures have been determined,[5,21] and even more closely related to $CH_3N(PF_2)_2Fe_2(CO)_7$, whose molecular structure has been inferred[6] from analytical and infrared data. A detailed comparison of the structures of $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**) and (1,2-diazine)$Fe_2(CO)_7$ (**7**) was presented by Cotton et al.[20] Here we make a similar detailed comparison between the more closely analogous compounds $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) and $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**). Bond lengths and valence angles (all uncorrected for thermal motion) are compared in Tables IV and V, respectively. Except for the Fe–P and Fe–Fe bonds, which are discussed further below, the corresponding bond lengths in **3** and **4**—that is, those that occupy corresponding positions *and* involve the same kinds of atoms—are not significantly different. The valence angles in **3** and **4** that correspond in the same sense are also remarkably close to each other. The two $P_2Fe_2(CO)_7$ moieties are strikingly similar.

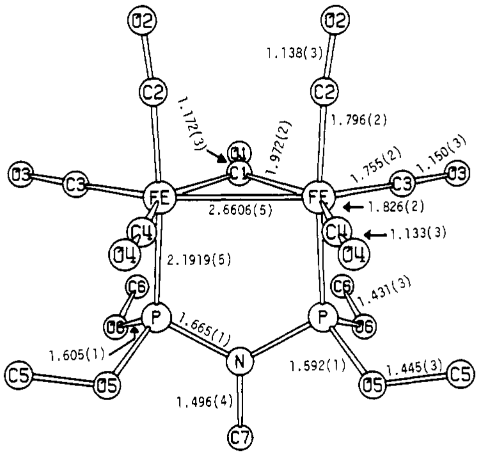

Figure 1. Drawing of the molecule of $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) with bond lengths (Å) and their esd's. The midpoint of the Fe–Fe bond and the atoms O(1), C(1), N, and C(7) lie on a crystallographic mirror plane.

Each of the Fe atoms may be regarded as six-coordinate, being bonded to P, C(1), C(2), C(3), and C(4) atoms and the other Fe atom. The major distortion from ideal octahedral geometry for the iron atoms arises from the constraints of the $Fe_2C(1)$ three-membered ring. The two Fe and two P atoms

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in the complex $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) are exactly coplanar (see plane 1 in Table VI in the supplementary material), because of the location of the molecule on a mirror plane, and the N atom is displaced only 0.016 (3) Å from the Fe_2P_2 plane. The seven-atom group made up of atom C(1) and two Fe, two C(3), and two C(4) atoms is very nearly plane (maximum displacement is 0.004 Å—see plane 2 in Table VI). The O(1), O(3), and O(4) atoms are within 0.05 Å of plane 2, which makes an angle of 89.31 (6)° with the plane of the group Fe_2P_2. The arrangement of atoms in these essentially orthogonal planes is a consequence of the octahedral iron geometry and the presence of the mirror plane.

In contrast with the structure of **3**, there is in the structure of **4** only an approximation to mirror symmetry, and the seven-atom group corresponding to the group used in defining plane 2 above is much further from planarity. The most striking difference between **3** and **4**, however, is the difference in the conformations of the two five-membered rings. The Fe_2P_2C ring in **4** is puckered, the carbon atom of the CH_2 group being 0.76 Å from the best plane through the nearly plane Fe_2P_2 group. The shape parameters ϕ, ρ, and $D(P\cdots P)$ used by Schubert et al.[21] in discussing the fitting of a metal–metal atom pair and a diphosphino ligand to each other to form a five-membered ring are 0°, 1.1 (2)°, and 2.893 (1) Å for **3** and 2°, 45°, and 2.709 (2) Å for **4**. In the tabulation in ref 21 of data for 23 complexes with five-membered rings similar to those in **3** and **4**, there is only one other complex, $\{HN[P(C_6H_5)_2]_2\}_2Co_2(CO)_6$, in which a ring displays the close approximation to C_{2v}-*mm*2 symmetry that the ring in **3** does. In all other cases in the tabulation either ϕ or σ is far from zero or both ϕ and σ are, and the rings are puckered. In $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$[4] each of the Co_2P_2N rings is also far from plane. The Co–Co distance in this complex is 2.698 (1) Å; the two sets of parameters ϕ, ρ, and $D(P\cdots P)$ are 41.2 (1)°, 16.3 (2)°, and 2.782 (2) Å and 34.6 (1)°, 20.6 (2)°, and 2.795 (2) Å.

The valence geometry of the nitrogen atom in $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) is essentially trigonal planar, indicating sp^2 hybridization, with each valence angle close to 120° and the N atom only 0.009 (3) Å from the plane of the carbon and phosphorus atoms attached to it. This geometry and the fact that the P–N bond length is only 1.665 (1) Å compared with the 1.76–1.80 Å expected from the sum of the single-bond covalent radii[21,22] suggest significant π-bond character in the P–N bond, as has been inferred for the P–N bonds in some other complexes involving M_2P_2N rings (M = Ag[21] and Co[23]). There is the same indication for the P–N bonds in $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$.

Schubert et al.[21] consider that double-bond character in the P–N bonds favors smaller ρ angles in M_2P_2N rings. Thus, the double-bond character and the presence of the bridging carbonyl, which favors planarity of the Fe_2P_2 group, together account for the nearly exact planarity of the Fe_2P_2N ring in $CH_3N[P(OCH_3)_2]_2Fe_2(CO)_7$. We may perhaps explain the shortening by ~0.05 Å of the Fe–Fe distance in **3** relative to that in **4** as the result of a compressive effect imposed by the ligand $CH_3N[P(OCH_3)_2]_2$ made possible by the P–N double-bond character that tends to maintain a plane ring. The ligand $CH_2[P(C_6H_5)]_2$ in **4** cannot effect the same compression because of the absence of double-bond character in the P–CH_2 bonds, and the bite of this ligand is more freely adjustable by rotation about the P–CH_2 bonds.[5] These arguments are weakened by the fact that the Co_2P_2N rings in the complex $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$ are not plane. However, in this case there is no bridging carbonyl, and the overall linkage pattern is sufficiently different from that in **3** that the same kind of ring conformation is not necessarily expected.

The Fe–P bond length of 2.1919 (5) Å in $CH_3[P(OCH_3)_2]_2Fe_2(CO)_7$ (**3**) is about 0.06 Å shorter than the Fe–P bond length in $CH_2[P(C_6H_5)_2]_2Fe_2(CO)_7$ (**4**), consistent with the expected superior π-acceptor property of the phosphorus atoms in **3**. The slight lengthening of bond Fe–C(2) in **3** expected to accompany shortening of the Fe–P bond in the trans position is not observed.

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Registry No. **3**, 82660-99-9; **5** (M = Cr), 82661-00-5; **5** (M = Mo), 82661-01-6; **6**, 82661-02-7; (norbornadiene)$Cr(CO)_4$, 12146-36-0; (norbornadiene)$Mo(CO)_4$, 12146-37-1; $Fe_2(CO)_9$, 15321-51-4; $Fe(CO)_5$, 13463-40-6.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table III), least-squares planes (Table VI), and observed and calculated values of F^2, with estimated standard errors of the former (19 pages). Ordering information is given on any current masthead page.

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