

Table IV. Comparative W-C and W-O Bond Distances (Å) in W(CO)₅ Derivatives

substituent	W-C _{eq}	W-C _{ax}	Δ	ref
O ₂ CH ⁻	2.037 (13)	1.911 (15)	0.126	<i>b</i>
O ₂ CCH ₃ ⁻	2.038 (18)	1.951 (6)	0.087	<i>c</i>
Ph ₂ P(O)NPPh ₃	2.035 (6)	1.946 (5)	0.089	<i>d</i>

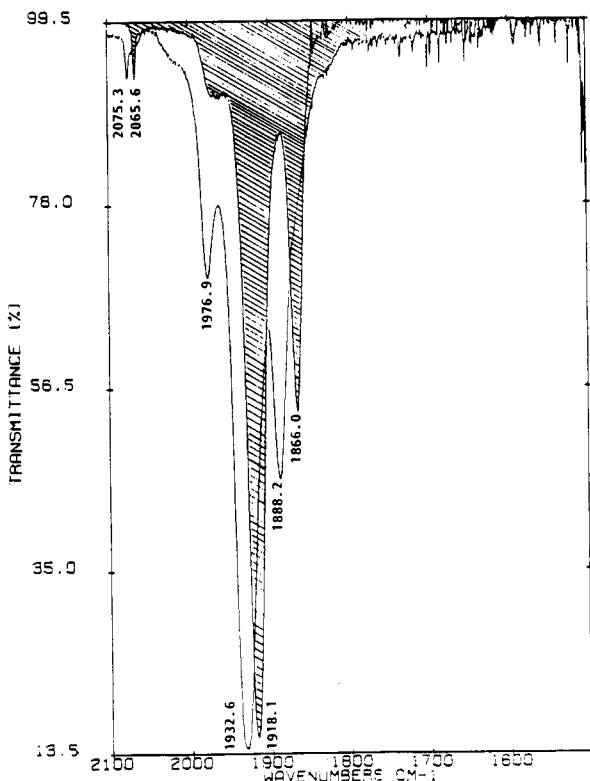
^aThis value represents the average of the four W-C_{eq} distances.

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^cCotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudarski, R. *Inorg. Chem.* **1982**, *21*, 1656. ^dThis work.

Table V. Rate Constants for Phosphine Oxide Displacement at Ambient Temperature

compd	solvent	CO pressure, psi	10 ³ k _{obsd} , min ⁻¹
W(CO) ₅ OP(Ph ₂)NPPh ₃	THF	14	0.26
	MeOH	14	1.76
	MeOH	110	14
W(CO) ₅ OPPh ₃	THF	14	2.49
	MeOH	14	4.88
W(CO) ₅ OPMe ₃	MeOH	14	3.26

**Figure 3.** Infrared spectra in $\nu(\text{CO})$ region of $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPh}_3$: (a) in THF (shaded); (b) in MeOH.

innocent ion, especially in the presence of good nucleophiles.

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Registry No. $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPh}_3$, 99618-35-6; $\text{W}(\text{CO})_5\text{THF}$, 36477-75-5; $\text{W}(\text{CO})_5\text{OPMe}_3$, 103620-60-6; $\text{W}(\text{CO})_5\text{OPPh}_3$, 103620-61-7; $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$, 2156-69-6; NaOCH_3 , 124-41-4; $[\text{PPN}][\text{Cl}]$, 21050-13-5; CO, 630-08-0.

Supplementary Material Available: Additional crystallographic data including complete tables of bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); a listing of observed vs. calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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Studies of the Synthesis and Thermolysis of Tris[tris(amino)phosphine]molybdenum Tricarbonyls: Synthesis of *fac*-[(*i*-PrNH)₃P]₃Mo(CO)₃

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We recently reported synthesis of the diphosphazane complex *cis*-PhN[P(NHPh)₂]₂Mo(CO)₄ by PhNH₂ elimination from the complex [(PhNH)₃P]₂Mo(CO)₄ in a metal-templated phosphorus-nitrogen bond condensation reaction.² In order to pursue this reaction type further, we undertook studies of the synthesis and thermolysis of selected tris[tris(amino)phosphine]molybdenum tricarbonyl complexes to determine if, in reactions analogous to those above, new metal-coordinated triphosphazanes might be obtained. The results of these studies are described below.

Experimental Section

Apparatus and Materials. All operations were carried out in N₂-flushed glovebags and standard vacuum line equipment.³ Infrared, ¹H NMR (90.0 MHz), and mass spectra were obtained with Beckman IR 4250, Varian EM390, and Varian MAT CH5 spectrometers, respectively. ³¹P NMR spectra were obtained on JEOL PFT-100 (40.5 MHz) and FX-90Q (36.4 MHz) spectrometers. ¹H and ³¹P NMR chemical shifts were measured relative to internal Me₄Si and H₃PO₄, respectively; shifts downfield from the standard are given + δ values. Single-crystal X-ray data were collected at ambient temperature with a Syntex PI automated diffractometer (Mo K α radiation, graphite monochromator).

fac-(PCl₃)₃Mo(CO)₃,⁴ *fac*-(PhPCl₂)₃Mo(CO)₃,⁴ (mes)Mo(CO)₃ (mes = mesitylene),⁵ and PhP(NHPh)₂⁶ were prepared and purified as described previously. Aniline (Mallinckrodt), Et₃N (Eastman Chemicals), and *i*-PrNH₂ (Matheson Coleman and Bell) were distilled from CaH₂. Benzene and toluene were distilled from Na/Pb alloy. CH₂Cl₂ and CHCl₃ were distilled from P₄O₁₀.

Reactions of *fac*-(PCl₃)₃Mo(CO)₃. (A) With *i*-PrNH₂. *i*-PrNH₂ (75 mmol) in toluene (30 mL) was added slowly to (PCl₃)₃Mo(CO)₃ (4.0 mmol) in 150 mL of toluene at 25 °C. After 8 h, *i*-PrNH₂Cl was filtered and the clear filtrate was passed through a 2-cm alumina column. The solution showed major and minor ³¹P NMR resonances at δ 109.5 [(*i*-PrNH)₃P]₃Mo(CO)₃ (1) and δ 110.7 (*i*-PrN[P(NH-*i*-Pr)₂Mo(CO)₄ (2)],² respectively. Evaporation of the solution and recrystallization of the solid from toluene yielded pure 1 (85% yield, based on Mo in reactant; mp 133–135 °C). Anal. Calcd for C₃₀H₇₂N₉P₃O₃Mo: C, 45.17; H, 9.03, N, 15.81; P, 11.67. Found: C, 43.38; H, 9.15; N, 15.16; P, 11.51. ¹H NMR (CDCl₃): δ 3.15–3.90 (m, area 9, CH), 1.10–1.55 (s, area 54, CH₃), 0.90 (m, area 9, NH). ³¹P NMR (C₆D₆): δ 109.5 (s). MS: parent and seven most intense envelopes at *m/e* (relative intensity) 685 (0.2, M⁺), 392 (7.8), 333 (6.2), 177 (5.1), 147 (17.5), 88 (13.9), 44 (100), 42 (64.8). IR (Nujol): characteristic absorptions at 3410 (w), 3370 (m), 1918 (s), 1815 (vs), 1166 (m), 1134 (s), 868 (m), and 791 cm⁻¹.

Under conditions identical with those above, except that reaction was allowed to proceed for 65 h at 25 °C, after recrystallization from benzene pure *i*-PrN[P(NH-*i*-Pr)₂Mo(CO)₄ (2); 57% yield, based on Mo in reactant; mp 116–118 °C) was obtained. Anal. Calcd for C₁₉H₃₉N₉P₃MoO₄: C, 40.79; H, 7.03; N, 12.52; P, 11.07. Found: C, 41.00; H, 7.14; N, 12.63; P, 11.11. ¹H NMR (CDCl₃): δ 3.50 (broad m, area 5, CH), 1.68 (d, area 4, *J* = 7.3 Hz, NH), 1.35 (d, area 6, *J* = 6.9 Hz, CH₃), 1.20 (d of d, area 24, *J* = 6.0 Hz, CH₃). ³¹P NMR (C₆D₆): δ 110.7 (s). MS: parent and six most intense envelopes at *m/e*

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Table I. Summary of Crystal Data for [(*i*-PrNH)₃P]₃Mo(CO)₃ (1)

formula	MoP ₃ N ₉ O ₃ C ₃₀ H ₇₂
mol wt	797
color of cryst	colorless
cryst dimens, mm	0.2 × 0.18 × 0.3
space group	R3
temp, °C	25
<i>a</i> , Å	19.906 (7)
<i>b</i> , Å	19.906 (7)
<i>c</i> , Å	9.441 (3)
Z, molecules/cell	3
vol, Å ³	3241 (2)
<i>d</i> _{calcd} , g/cm ³	1.23
<i>d</i> _{obsd} , g/cm ³	1.22
wavelength, Å	0.710 69
linear abs coeff, cm ⁻¹	4.5
scan mode	θ-2θ
scan speed, deg/min	2-24
2θ, min and max, deg	3.0-35.0
reflecons	
total	1815
unique	635
obsd, <i>I</i> ₀ > 3.0σ(<i>I</i> ₀)	432
R ^o	
R _w ^a	
goodness of fit ^a	1.60

^aThe quantity minimized in the least-squares procedure was $\sum w \cdot (|F_o| - |F_c|)^2$. $R = \sigma |F_o| - |F_c| / \sum |F_o|$ and $R_w = [\sum w |F_o| - |F_c|]^2 / \sum w F_o^2$. The goodness of fit is $[\sum w (|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{var}})]^{1/2}$. The weights, *w*, were calculated from counting statistics as $w = 1/\sigma^2(F_o)$.

(relative intensity) 563 (8.6, M⁺), 446 (27.7), 389 (45.2), 331 (43.9), 90 (63.0), 58 (33.7), and 44 (100). IR (Nujol): characteristic absorptions at 3368 (m), 2013 (m), 1914 (s), 1890 (s), 1854 (s), 1395 (m), 1364 (m), 1025 (m), 887 (m), 862 (m), 802 (m), 620 (m), and 578 (m) cm⁻¹.

(B) With PhNH₂. PhNH₂ (20 mmol) in benzene (10 mL) was added slowly to (PCl₃)₃Mo(CO)₃ (2.3 mmol) and Et₃N (24 mmol) in benzene at 0 °C. After 4-8 h at 25 °C, the Et₃NHCl was filtered and the filtrate was slowly concentrated in vacuo at 25 °C. Initially, the reaction solution exhibited two ³¹P NMR spectral resonances at δ 96.7 (*cis*-PhN[Ph(NHPh)]₂Mo(CO)₄ (3))² and δ 107.3 (4), in area ratios ranging from 1:4.5 to 1:6.0. Upon solvent removal the δ 96.7 resonance increased and the δ 107.3 resonance decreased. The relative area of the δ 96.7 and 107.3 peaks, in the final reaction solid when redissolved in benzene, was approximately 8.5:1. Recrystallization from toluene yielded pure 3 (characterized by IR, MS, and ³¹P NMR spectra). Attempts to isolate 4 by crystallization or thin-layer chromatography were unsuccessful.

Reaction of *fac*-(PhPCl₂)₃Mo(CO)₃ with PhNH₂. PhNH₂ (5.5 mmol) and Et₃N (5.8 mmol) were added to (PhPCl₂)₃Mo(CO)₃ (0.32 mmol) in toluene. After 15 h at 25 °C, Et₃NHCl was filtered. The filtrate exhibited resonances at δ 171.8 (area 2, unreacted (PhPCl₂)₃Mo(CO)₃), 88.6 (area 4, [PhP(NHPh)]₂Mo(CO)₄ (5)),² 90.1 (area 1, 7), and 45.7 (area 5, PhP(NHPh)₂). After 18 h at 100 °C, 5 and 7 disappeared and two new equal-area peaks at δ 98.4 and 97.5 (PhN[Ph(NHPh)]₂Mo(CO)₄ (6))² appeared. 5 and 6 could be isolated by fractional crystallization; however, attempts to isolate other products failed.

Crystallographic Study. Crystal data and refinement details are summarized in Table I. All parameters were determined on the diffractometer and refined by least-squares fit to 15 centered reflections. Because of concern for the stability of 1, the backgrounds were collected for only one-fourth of the scan time and the data were collected in shells. At the end of data collection to 35° (2θ), the decline in intensity was 23%. Measurements at higher 2θ values (to 50°) were abandoned because even more significant decline occurred. Data were corrected for Lorentz and polarization but not absorption effects. Equivalent reflections were averaged (*R*_{av} = 0.048). The Mo and P atoms were located by heavy-atom methods using a Patterson map; remaining atoms were located from a three-dimensional difference map. The three parts of the molecule are related by a 3-fold rotation axis. Only the Mo and P atoms were treated anisotropically. The H atoms were located in three-dimensional difference maps and included in fixed, idealized positions, with temperature factors set to be 1 Å² greater than those of the atom to which they were attached. Scattering factors were those for neutral atoms.⁷ Final pos-

Table II. Positional Parameters for [(*i*-PrNH)₃P]₃Mo(CO)₃ (1)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mo	0	0	0.200
P	0.1232 (3) ^a	0.0457 (2)	0.3446 (4)
C(1)	0.037 (1)	-0.049 (1)	0.077 (2)
N(1)	0.1962 (7)	0.1074 (7)	0.242 (1)
N(2)	0.1604 (6)	-0.0084 (6)	0.399 (1)
N(3)	0.1175 (6)	0.0781 (6)	0.502 (1)
C(11)	0.2817 (8)	0.1475 (9)	0.268 (2)
C(12)	0.315 (1)	0.234 (1)	0.294 (2)
C(13)	0.320 (1)	0.140 (1)	0.137 (2)
C(21)	0.1807 (8)	-0.0559 (9)	0.305 (2)
C(22)	0.258 (1)	-0.048 (1)	0.356 (2)
C(23)	0.119 (1)	-0.1388 (9)	0.310 (2)
C(31)	0.1778 (8)	0.1069 (8)	0.618 (2)
C(32)	0.1930 (8)	0.1879 (9)	0.667 (2)
C(33)	0.1503 (9)	0.0511 (9)	0.742 (2)
O(1)	0.0629 (6)	-0.0796 (7)	-0.002 (1)

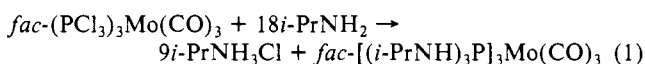
^aEstimated standard deviations shown in parentheses in tables are of the least significant digits of the preceding number.

itional parameters are given in Table II. All programs were contained in or derived from Syntex (now Nicolet) data reduction routines, the MULTAN 78 package,⁸ and the Northwestern University crystallographic computing package of Dr. J. A. Ibers.

To determine absolute configuration, four cycles of refinement were performed with *hkl* values converted to *h \bar{k} l*. A comparison of *R* factors showed the original geometry to be the absolute conformation to at least the 99.5% level of certainty.⁹ A comparison of the calculated and observed structure factor amplitudes of a limited number of Friedel pairs was consistent with this conclusion.

Results and Discussion

Reaction of *i*-PrNH₂ with *fac*-(PCl₃)₃Mo(CO)₃ results in elimination of *i*-PrNH₃Cl and formation of *fac*-[(*i*-PrNH)₃P]₃Mo(CO)₃ (1)



a unique example of a tris(tris(amino)phosphine) complex. Previous studies of Mo(CO)₆ or (cyclohept)Mo(CO)₃ (cyclohept = cycloheptatriene) reactions with (Me₂N)₃P yielded no tris-(phosphine) products; only bis(phosphine) tetracarbonyls were obtained.^{10,11} The reaction in eq 1 is analogous to those between (CO)₅MoPCl₂ and RNH₂ (R = H, Me, *i*-Pr, Ph, NHPH), which yield mono(phosphine) complexes, (CO)₅MoP(NHR)₃.¹²⁻¹⁵ During a longer reaction period, 60 h at 25 °C, *i*-PrNH₂ and (PCl₃)₃Mo(CO)₃ react further to the diphosphazane complex *i*-PrN[*i*-PrNH)₂P]₂Mo(CO)₄ (2). No evidence was obtained for formation of coordinated triphosphazane products.

The PhNH₂-(PCl₃)₃Mo(CO)₃ and PhNH₂-(PhPCl₂)₃Mo(CO)₃ reactions in the presence of Et₃N proceed less cleanly to mixtures that also ultimately yield the previously reported diphosphazane complexes PhN[(PhNH)₂P]₂Mo(CO)₄ (3) and PhN[Ph(NHPh)]₂Mo(CO)₄ (6) as the major isolatable Mo-containing products.² Initially, the PhNH₂-(PCl₃)₃Mo(CO)₃ reaction mixture exhibits a ³¹P NMR spectral resonance at δ 107.3, which upon heating and/or solvent removal disappears as the resonance due to 3 grows. The δ 107.3 peak is tentatively attributed to [(PhNH)₃P]₃Mo(CO)₃ (4), because of the close coincidence of

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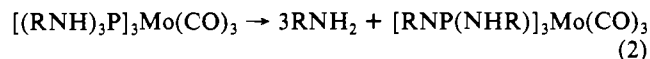
Table III. Selected Structural Parameters for $[(i\text{-PrNH})_3\text{P}]_3\text{Mo}(\text{CO})_3$ (**1**)

(a) Bond Lengths (Å)			
Mo-P	2.545 (7)	N(1)-C(11)	1.49 (2)
Mo-C(1)	1.90 (2)	N(2)-C(21)	1.50 (2)
P-N(1)	1.67 (1)	N(3)-C(31)	1.51 (2)
P-N(2)	1.67 (1)	C(1)-O(1)	1.21 (2)
P-N(3)	1.65 (2)		
(b) Bond Angles (deg)			
Mo-P-N(1)	106.4 (5)	C(1)-Mo-C(1)'	86.6 (7)
Mo-P-N(2)	126.6 (5)	N(1)-P-N(2)	98.7 (6)
Mo-P-N(3)	112.4 (4)	N(1)-P-N(3)	116.2 (6)
Mo-C(1)-O(1)	179 (2)	N(2)-P-N(3)	96.5 (6)
P-Mo-P'	93.9 (2)	P-N(1)-C(11)	130 (1)
P-Mo-C(1)	87.3 (5)	P-N(2)-C(21)	124.8 (9)
P-Mo-C(1)'	92.0 (6)	P-N(3)-C(31)	127.4 (9)
P-Mo-C(1)''	173.8 (5)		

its ^{31}P NMR resonance with that of **1** (δ 109.5).

The $\text{PhNH}_2\text{-(PhPCl}_2)_3\text{Mo}(\text{CO})_3$ reaction initially yields one major product (δ 90.1; **7**) along with $[\text{PhP}(\text{NHPH})_2]_2\text{Mo}(\text{CO})_4$ (**5**) and $\text{PhP}(\text{NHPH})_2$. Compound **7** is thermally unstable; consequently, we were unable to separate and characterize it completely. Since the thermal behavior of **7** parallels closely that of **4** from the $\text{PhNH}_2\text{-(PCl}_3)_3\text{Mo}(\text{CO})_3$ reaction, **7** is characterized tentatively as $[\text{PhP}(\text{NHPH})_2]_3\text{Mo}(\text{CO})_3$. Other resonances appear in the reaction after heating at 100 °C for 18 h; however, we were unable to characterize products further.

Although the tris(tris(amino)phosphine) complex **1** forms, as perhaps also do the analogue compounds **4** and **7**, none appear inclined to undergo metal-templated P-N bond condensation to form either cyclic or acyclic triphosphazane products, e.g. as shown in eq 2. The compounds studied exhibit a range of stabilities;



1 is most thermally stable whereas **4** and **7** are less so. In every case, the diphosphazane complexes were the major products. These reactions do involve P-N bond condensation probably on the metal centers, but only to the extent of forming P-N-P skeletal units. Apparently, formation of triphosphazanes is disfavored, perhaps because of steric crowding in the final complex.

Compound **1** was characterized in solution and in the solid by spectral data (MS, IR, ^1H and ^{31}P NMR) and a single-crystal X-ray analysis. The structure of **1** is shown in Figure 1. Selected intramolecular bond parameters are listed in Table III. A complete listing of structural parameters is in the supplementary material. Three $(i\text{-PrNH})_3\text{P}$ molecules are facially coordinated to the $\text{Mo}(\text{CO})_3$ unit, forming a complex with crystallographic and molecular point group C_3 symmetry. The presence of a singlet ^{31}P NMR resonance and two characteristic carbonyl IR absorptions¹⁶ confirms the facial isomeric structure of **1** in solution also. The mean P-N bond distance of 1.67 (1) Å is within the 1.66–1.70-Å range of P-N bonds in other (aminophosphine)molybdenum carbonyl complexes^{17–19} and is shorter than the distances of 1.69–1.73 Å reported for uncoordinated tris(amino)phosphines $(\text{PhNH})_3\text{P}$,^{20,21} $[(\text{CH}_2)_3\text{N}]_3\text{P}$,²² and $(\text{Me}_2\text{N})_3\text{P}$.²³ The Mo-P distance of 2.55 Å is typical for phosphine-Mo complexes; how-

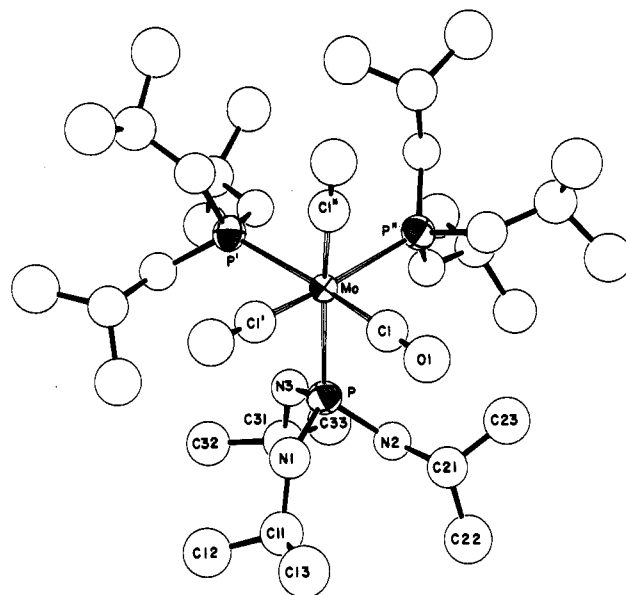


Figure 1. Structure of *fac*- $[(i\text{-PrNH})_3\text{P}]_3\text{Mo}(\text{CO})_3$ (**1**) showing the atom-numbering scheme. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

ever, the 1.90 Å Mo-C distance is shorter than usual (e.g. 1.97–2.05 Å).^{24–26} The *cis* $\angle\text{P-Mo-P}$ (94°) and $\angle\text{C-Mo-C}$ (87°) angles as expected²⁷ are greater than and less than 90°, respectively, perhaps the result of crowding among the facially coordinated $(i\text{-PrNH})_3\text{P}$ molecules. In light of this crowding, the relatively high stability of **1** is surprising. In contrast, a molybdenum tricarbonyl unit will not accommodate three bulky tricyclohexylphosphine substituents^{28,29} but instead forms five-coordinated complexes.²⁹

The PN_3 unit conformation of each tris(amino)phosphine moiety is of the distorted C_3 type, similar to that observed previously in other tris(amino)phosphine compounds.^{17,18,22} In the limiting C_3 conformation, the phosphorus lone-pair electrons are parallel to one and perpendicular to two nitrogen lone-pair electrons.³⁰ In **1**, the torsion angles around P-N bonds, C(21)-N(2)-P-Mo, C(11)-N(1)-P-Mo, and C(31)-N(3)-P-Mo, are 56, -175, and 178°, respectively.³¹

$(\text{RNH})_3\text{P}$ (R = H or alkyl), thermally unstable when uncomplexed,^{12–15,23} is greatly stabilized by coordination to Mo carbonyl moieties. The $(\text{PhNH})_3\text{P}$ appears stabilized to a lesser degree, since in both **4** and the previously reported $[\text{P}(\text{NHPH})_2]_3\text{Mo}(\text{CO})_4$,² rapid PhNH_2 elimination occurs to form the diphosphazane, $\text{PhN}[(\text{PhNH})_2\text{P}]_2\text{Mo}(\text{CO})_4$ (**3**). These metal-templated condensations resemble that reported for $[(\text{PF}_2)_2\text{NPh}]_3\text{Mo}(\text{CO})_3$, a species that eliminates PF_3 to form the novel complex $(\text{PF}_2\text{NPh})_2\text{PMo}(\text{CO})_3$.³² Why unsubstituted or alkyl-substituted aminophosphines might be stabilized to a greater degree than arylaminophosphines is unclear. Studies of this and ways to

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catalyze the condensation reactions of coordinated alkylamino-phosphines are in progress.

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Supplementary Material Available: Listings of thermal parameters, positional and thermal parameters for hydrogen atoms, structural parameters, planes, equations and deviations from planes, and torsion angles and a crystal packing diagram (6 pages); a table of structure factors (2 pages). Ordering information is given on any current masthead page.

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Mass Spectra and ⁹Be NMR Spectra of Partially Fluorinated β -Diketonate Complexes of Beryllium

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Numerous mass spectral studies of metal complexes of β -diketonates have appeared, with acetylacetonate complexes being the most extensively studied.¹⁻⁶ Comparative studies on the effect of the metal^{4b,5} and on the influence of the R group of the β -diketonate ligand⁸ on the mass spectral fragmentation patterns have also been reported. However, data are sparse on the mass spectra of beryllium β -diketonates,⁴ with no results reported on fluorinated β -diketonate-beryllium complexes.

We describe here the mass spectra of several fluorinated β -diketonate-beryllium complexes, having methyl, phenyl and aryl substituents. Transfer of a fluorine atom from ligand to metal is observed, which follows from hard-soft acid-base theory.

The ⁹Be NMR spectra of the complexes are also reported. Some trends in the chemical shifts of the compounds can be discerned. The ¹H, ¹³C, and ¹⁹F NMR spectra of these same β -diketonate beryllium complexes have already been reported.⁹

Results and Discussion

The structure of the beryllium β -diketonate complexes is shown in Figure 1, with the substituent groups listed in Table I. The geometry at the beryllium atom is tetrahedral with the formal

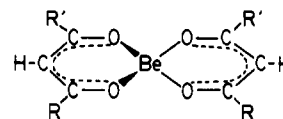


Figure 1. Structure of the beryllium- β -diketonate complexes. The geometry at beryllium is tetrahedral.

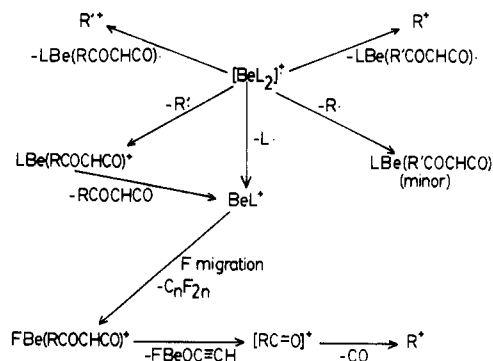


Figure 2. Major fragmentation pathways observed in the mass spectra of the partially fluorinated β -diketonate complexes of beryllium.

Table I. Mass and Relative Intensity of Molecular Ions of Be(RCOCHCOR')₂

compd no.	R	R'	M ⁺ m/e	rel intens, %
1	CH ₃	CF ₃	315	30.8
2	C ₆ H ₅	CF ₃	439	36.0
3	2'-C ₄ H ₃ S	CF ₃	451	32.1
4	2'-C ₄ H ₃ O	CF ₃	419	37.3
5	C ₆ H ₅	C ₂ F ₅	539	13.3
6	2'-C ₄ H ₃ S	C ₂ F ₅	551	10.6
7	C ₆ H ₅	C ₃ F ₇	639	4.9
8	2'-C ₄ H ₃ S	C ₃ F ₇	651	6.0

symmetry as *D*_{2d} for Be(acac)₂ and Be(hfac)₂, and *C*₂ for the unsymmetrically substituted β -diketonate beryllium complexes. Thus these latter chelates are rendered dissymmetric.⁹ The appearance of the mass spectra of these complexes is simplified by there being only single isotopes for beryllium and fluorine, and major isotopes for carbon, oxygen, and hydrogen that have only minor contributions from secondary isotopes. Thus, the spectra appear stark, with a single peak for each ion in the spectrum. The molecular ion is observed for each complex. The mass and relative intensity of the molecular ions for each complex are listed in Table I. The relative intensities of prominent ions are given in Table II. The major fragmentation pathways are shown in Figure 2.

Initial fragmentation of the molecular ion proceeds by loss of R', the fluorinated substituent on the diketone ligand. Peaks appear at masses corresponding to M⁺ - R, which is the loss of the nonfluorinated substituent. However, these peaks are either quite small (compounds 1-4, 6, 8) or they are absent altogether (compounds 5 and 7). Loss of a CF₃ radical is preferred to loss of a CH₃ radical due to higher stability of the CF₃ radical.² This trend appears to be general for fluorinated ligands over non-fluorinated ones. Indeed, the stability of the phenyl radical compared to \cdot C₂F₅ or \cdot C₃F₇ is so small that M⁺ - R is not observed for compounds 5 and 7. The parent ion may cleave at the same bond, but in an alternate fashion as shown in Figure 2, creating R⁺ and LBe(RCOCHCO)⁺. However, rupture of this bond appears to favor formation of LBe(RCOCHCO)⁺ and R' over this alternate cleavage as demonstrated by a comparison of the intensities of R⁺ and M⁺ - R' listed in Table II.

The next major peak in the mass spectrum at higher mass corresponds to M⁺ - L, where one β -diketonate ligand has been lost from the parent. Loss of an entire ligand, as a radical, is commonly observed in β -diketonate-metal complexes.²⁻⁷ Loss of the ligand as a radical creates an even electron ion, BeL⁺, which is then susceptible to fragmentation by loss of neutral even-electron species.³ This general phenomenon is observed in the mass spectra

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