Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Preparation and Characterization of Triphospholene Complexes of Zerovalent Platinum: Crystal and Molecular Structure of $[\mathrm{Pt}\{(\mathrm{CF_3})\overline{\mathrm{P(CF_3)P(CF_3)PC(CF_3)=C}}(\mathrm{CF_3})\}(\mathrm{PPh_3})_2]$

Ian G. Phillips, Richard G. Ball, and Ronald G. Cavell*

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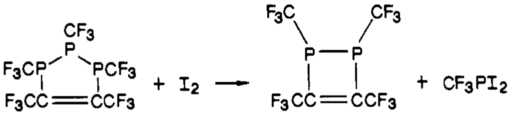
The triphospholene $(\mathrm{CF_3})\overline{\mathrm{P(CF_3)P(CF_3)P(CF_3)C=C}}(\mathrm{CF_3})$ (L) reacts with $[\mathrm{Pt(PEt_3)_4}]$ or $[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})(\mathrm{PPh_3})_2]$ at -50 °C in chloroform or toluene solution to give unidentified red complexes that decompose at +25 °C to give the complexes $[\mathrm{Pt(L)(PR_3)_2}]$ (R = Et (I), Ph (II)). The latter complex (II) (η^2(C_4,C_5)-1,2,3,4,5-pentakis(trifluoromethyl)-1,2,3-triphosphol-4-ene)bis(triphenylphosphane)platinum(0), $[\mathrm{Pt}\{(\mathrm{CF_3})\overline{\mathrm{P(CF_3)P(CF_3)PC(CF_3)=C}}(\mathrm{CF_3})\}(\mathrm{PPh_3})_2]$, crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell of dimensions a = 12.244 (2) Å, b = 17.400 (3) Å, c = 21.209 (5) Å, and β = 96.70 (2)°. The structural determination that gave the positional parameters for all the non-hydrogen atoms converged to $R_1 = 0.038$ and $R_2 = 0.029$ for 7049 reflections having $2\theta_{\mathrm{Mo\,K\alpha}} \leq 56.00°$ and $I > 3\sigma(I)$. The structure analysis revealed that the triphospholene ligand in II is almost planar and is coordinated to the metal through its olefinic functional group. Principal bond lengths in II are as follows: C=C, 1.490 (9) Å; P-P, 2.175 (3) and 2.191 (4) Å; Pt-C(olefin)$_{\mathrm{av}}$, 2.096 (6); and P-C(olefin)$_{\mathrm{av}}$, 1.837 (8) Å. One fluorine of the unique $\mathrm{PCF_3}$ group of the coordinated ring approaches to within 3.309 Å of the metal. This agostic Pt-F interaction appears to persist in solution in both complexes as indicated by an unusual spin-spin coupling constant between Pt and F in the ^{19}F NMR spectrum and an anomalously large shift to low field of the phosphorus resonance for the phosphorus atom with which the coupled fluorines are associated.

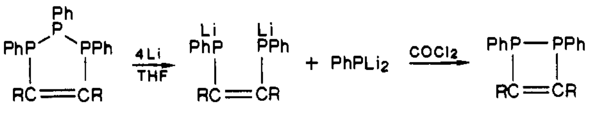
Introduction

In 1964 Mahler reported[1] the preparation of 1,2,3,4,5-pentakis(trifluoromethyl)-1,2,3-triphosphol-4-ene (L) as one of two products in the reaction of $[(\mathrm{CF_3})\mathrm{P}]_{4,5}$ with excess $\mathrm{CF_3C{\equiv}CCF_3}$ at 170 °C. Little chemistry of this interesting compound has been reported, though in the original report L was shown to react cleanly with iodine at elevated temperature to give a diphosphetene (eq 1). The anion radical of L can be produced by electrolytic reduction in various solvents at low temperatures,[2] and electron spin resonance spectra of the resultant species are consistent with a ring geometry that is planar about the olefinic functional group and is folded across the P1-P3 axis of an *all-trans*-triphospholene radical anion.



(1)

More recently Mathey et al.[3] have demonstrated the synthetic utility of several triphospholenes prepared from pyrolysis of $[\mathrm{PhP}]_5$ with various acetylenes in sealed tubes. Lithium cleavage followed by ring closure with phosgene converts triphospholenes to diphosphetenes, thereby permitting access to diphosphetenes that could not be prepared by the pyrolysis route (eq 2). A related triphospholene, 1,2,3,4,5-pentaphenyl-1,2,3-triphosphol-4-ene, was first prepared in low yield as its 1,3-disulfide by Ecker and Schmidt.[4] The coordination chemistry of triphospholenes seems not to have been studied, and herein we report our results of the study of the reaction of a trifluoromethyl triphospholene (L) with zerovalent platinum complexes.



(2)

R = Ph, 25%; R = Et, 22%

Experimental Section

All reactions were carried out in sealed tubes, and standard vacuum line techniques[5] were employed throughout for the manipulation of volatile materials. Air-sensitive solids were handled under nitrogen by using standard Schlenk techniques.[5] Chloroform ($\mathrm{CDCl_3}$ or $\mathrm{CHCl_3}$) and toluene-d_8 were stored over $\mathrm{P_2O_5}$ and distilled as required. $[(\mathrm{CF_3})\mathrm{P}]_{4,5}$,[6] $[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})(\mathrm{PPh_3})_2]$,[7] and $[\mathrm{Pt(PEt_3)_4}]$[8] were prepared by literature methods. With use of Mahler's preparation,[1] $(\mathrm{CF_3P})_3(\mathrm{CF_3C})_2$, L, was obtained as a mixture with $[(\mathrm{CF_3})\mathrm{P}]_{4,5}$, inseparable by fractional distillation. In a single experiment repeated removal of colorless solids over a period of 3 months gave a >95% enriched sample of L (estimated from ^{19}F NMR spectra of the neat liquid).

^{19}F and ^{31}P NMR spectra spectra were recorded on $\mathrm{CDCl_3}$ solutions with a Bruker WP400 instrument operating at 376.44 and 161.98 MHz, respectively. Shifts are measured by using the ^{2}D lock signal and quoted with reference to $\mathrm{CFCl_3}$ or 85% $\mathrm{H_3PO_4}$. ^{19}F NMR spectra of neat samples of L, containing less than 5% impurity (by NMR) of unidentified fluorine species, were recorded on a Bruker WP80 spectrometer. Chemical shifts were measured in this case relative to an external $\mathrm{CFCl_3/CDCl_3}$ reference.

Preparation of $[\mathrm{Pt}\{(\mathrm{CF_3})\overline{\mathrm{P(CF_3)P(CF_3)PC(CF_3)=C}}(\mathrm{CF_3})\}(\mathrm{PEt_3})_2]$ (I). The phospholene ligand L (70 mg, 0.15 mmol) was distilled onto a frozen toluene-d_8 solution of $[\mathrm{Pt(PEt_3)_4}]$ (93 mg, 0.14 mmol) in a 5-mm NMR tube. The tube was then warmed to -78 °C, whereupon a red coloration developed as the reactants mixed. A +25 °C the solution color had changed irreversibly to pale yellow. Slow evaporation from a $\mathrm{CHCl_3}$ solution of the reaction residue gave the product as yellow microprisms, which were separated by decantation of the mother liquors, washed with ether, and dried in vacuo (0.001 mm, 2 h): mp 170-170.5 °C dec; yield 94 mg (50%). Anal. Calcd for $\mathrm{C_{19}H_{30}F_{15}P_5Pt}$: C, 25.54; H, 3.38. Found: C, 25.62; H, 3.46.

Preparation of $[\mathrm{Pt}\{(\mathrm{CF_3})\overline{\mathrm{P(CF_3)P(CF_3)PC(CF_3)=C}}(\mathrm{CF_3})\}(\mathrm{PPh_3})_2]$ (II). In a similar fashion the reaction of L (49 mg, 0.11, mmol) and $[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})(\mathrm{PPh_3})_2]$ (81 mg, 0.11 mmol) in $\mathrm{CDCl_3}$ gave II. Warming the frozen reactants to -60 °C caused rapid evolution of ethylene and the development of a deep red coloration in the solution. At +25 °C II crystallized from the reaction mixture as colorless prisms that were separated by decantation, washed with ether, and dried in vacuo (0.001 mm, 2 h): mp 175-176.5 °C dec; yield 30 mg (26%). Subsequent batches of crystalline solid were obtained by slow evaporation of solvent from the mother liquors. Anal. Calcd for $\mathrm{C_{43}H_{30}F_{15}P_5Pt}$: C, 43.71; H, 2.56; M_r, 1181.65. Found: C, 43.68; H, 2.54; M_r, 1170 (benzene), 1181.65 (structural determination). Compound II was similarly prepared in toluene in comparable yields.

X-ray Data Collection and Structure Solution for Compound II.[9] Data were collected on an Enraf-Nonius CAD 4F diffractometer at +25 °C by using a crystal mounted in a nonspecific orientation. (See Table I for crystal data and intensity collection details.) The automatic peak search

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(9) The X-ray crystallographic study for this molecule comprises report number S.R.030122-04-85 of the Structure Determination Laboratory, Department of Chemistry, University of Alberta. See paragraph at the end of the paper regarding supplementary material.

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Table I. Crystal Data and Details of Intensity Collection for II

mol formula	$C_{43}H_{30}F_{15}P_5Pt$
fw	1181.65
cryst shape	prism
dryst size, mm	0.19 × 0.17 × 0.43
syst absences	$h0l$ ($h + l$ odd), $0k0$ (k odd)
space group	monoclinic, $P2_1/n$
radiation	Mo Kα (λ = 0.7107 Å), graphite monochromator
unit cell params	
a, Å	12.244 (2)
b, Å	17.400 (3)
c, Å	21.209 (5)
β, deg	96.70 (2)
V, Å^3	4488
Z	4
ρ_{calcd}, g cm^{-3}	1.749
linear abs coeff, μ, cm^{-1}	34.26
max 2θ rflns collcd, deg	56.00
takeoff angle, deg	3.0
detector aperture, mm	2.40 (horiz), 4.0 (vert)
cryst to detector dist, mm	205
scan type	ω–2θ
scan rate, deg/min	10.1–1.5
scan width, deg	0.80 + 0.35 tan θ
total no. of rflns collcd	11 654
no. of indep rflns	10 788
no. of observns ($I > 3.0\sigma(I)$)	7049
no. of variables	577
final R_1, R_2[a]	0.038, 0.029

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

and reflection indexing programs[10] in conjunction with a cell reduction program established the crystal system, and the systematic absences unambiguously established the space group[11] as $P2_1/n$. Cell constants were obtained from a least-squares refinement of the setting angles of 22 reflections in the range $16 < 2\theta < 28°$.

The intensity data were collected by using an ω–2θ scan with variable scan speeds chosen to give $\sigma(I)/I \leq 0.05$ within a time limit of 60 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. Three reflections were chosen as standards and were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. The standards showed a mean change in intensity of 9.4% over the time of data collection, for which no correction was applied to the data.

The data were corrected for Lorentz, polarization, and background effects.[12] Data were reduced in the usual manner by using a value of $p = 0.04$ to downweight intense reflections. The data were corrected for absorption effects by using an empirical correction based on the absorption surface method of Walker and Stuart.[13] The maximum and minimum correction coefficients applied to F_o were 1.1723 and 0.8465, respectively. After equivalent forms were averaged and any systematically absent data were rejected, there were 10 788 unique reflections, of which 7049, having $I > 3\sigma(I)$, were used in the structure solution and refinements.

The structure was solved by using a three-dimensional Patterson synthesis, which gave the positional parameters for the Pt atom. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis. Hydrogen atoms were not included in the refinement due to limitations in the computational ability at hand.

The refinement was carried out by using full-matrix least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral atom scattering factors[14] and the anomalous dispersion terms for all non-hydrogen atoms[15] were obtained from the usual sources. In the final model all atoms were allowed anisotropic thermal parameters.

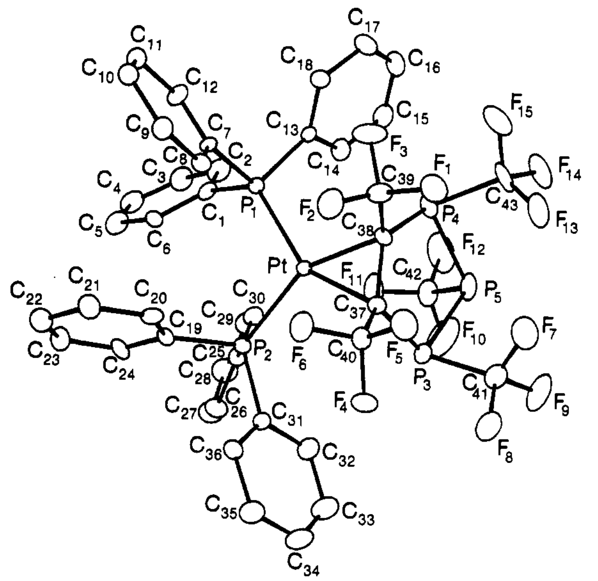

Figure 1. Perspective view of the molecular structure of II showing the numbering scheme. All non-hydrogen atoms are shown as 20% probability ellipsoids.

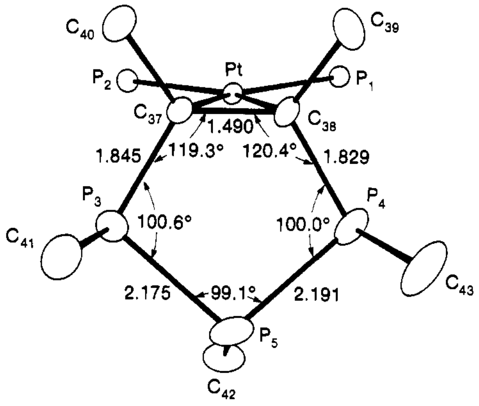

Figure 2. View of the core of the molecule showing important bond angles and lengths in the ring and the plane surrounding the Pt atom.

An analysis of R_2 in terms of R_0, λ^{-1} sin θ, and various combinations of Miller indices showed no unusual trends. The highest peak in the final difference Fourier map has an electron density of 0.7 (1) e Å^{-3} and represents the H atom attached to C(10).

The positional parameters for compound II are given in Table II. Additional information is given later and is given as supplementary material.

Results and Discussion

The cyclopolyphosphane heterocycle 1,2,3,4,5-pentakis(trifluoromethyl)-1,2,3-triphosphol-4-ene (L) reacts with $[Pt(PEt_3)_4]$ or $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ in toluene or chloroform solution at low temperatures to yield red species. At this stage ^{19}F and ^{31}P NMR spectra of the mixtures were broad and uninformative due, in part, to suspended solids in the reaction mixture. When the solution was warmed to +25 °C, the thermally unstable red species decomposed to give pale yellow or colorless solutions of a single product, from which the monomeric complexes $[Pt(L)(PR_3)_2]$ (R = Et, I; R = Ph, II), were respectively obtained.

In each case the ^{31}P NMR spectra show three signals, a broad doublet (intensity 2), a sharp triplet of multiplets (intensity 1), and a broad singlet (intensity 2) with ^{195}Pt satellites ($^1J_{PPt}$ = 3332 (I) and 3518 (II) Hz). Only the last signals, assigned to the

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[10] The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications and additions.

[11] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I.

[12] The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package by B. A. Frenz (*Computing in Crystallography*; Delft University Press: Delft, Holland, 1978, pp 64–71) and several locally written or modified programs.

[13] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor., Gen. Crystallogr.* **1983**, *39*, 158.

[14] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

[15] Reference 14, Table 2.31.

Table II. Final Positional ($\times 10^4$) and Thermal Parameters ($\times 10^2$) for Non-Hydrogen Atoms of II[a,b]

atom	x	y	z	U,[c] Å^2
Pt	2396.7 (2)	2232.8 (1)	3748.65 (9)	2.563 (3)
P(1)	516 (1)	2087.3 (7)	3820.5 (6)	2.94 (4)
P(2)	3111 (1)	2607.5 (8)	4766.6 (6)	3.38 (4)
P(3)	4731 (1)	1524 (1)	3424.3 (7)	4.84 (5)
P(4)	2323 (1)	997.2 (9)	2660.8 (7)	4.95 (5)
P(5)	3907 (2)	492 (1)	3034.5 (8)	5.76 (5)
F(1)	2524 (3)	2495 (2)	1744 (1)	6.8 (1)
F(2)	2019 (3)	3263 (2)	2427 (2)	6.7 (1)
F(3)	1021 (3)	2301 (3)	2130 (2)	8.1 (1)
F(4)	5185 (3)	3083 (2)	3432 (2)	6.4 (1)
F(5)	4383 (3)	3172 (2)	2487 (2)	6.7 (1)
F(6)	3626 (3)	3629 (2)	3267 (2)	6.7 (1)
F(7)	5280 (4)	1616 (3)	2186 (3)	11.0 (2)
F(8)	6444 (3)	2097 (3)	2873 (2)	12.5 (2)
F(9)	6274 (4)	876 (3)	2796 (3)	12.6 (2)
F(10)	4406 (5)	−260 (3)	4094 (3)	16.0 (2)
F(11)	3026 (4)	443 (3)	4177 (2)	9.8 (2)
F(12)	2846 (5)	−551 (3)	3648 (2)	14.0 (2)
F(13)	3437 (4)	1027 (3)	1573 (2)	9.3 (2)
F(14)	2601 (5)	−6 (3)	1755 (2)	11.2 (2)
F(15)	1665 (5)	998 (3)	1417 (2)	11.6 (2)
C(1)	−45 (4)	1909 (3)	4566 (2)	4.1 (2)
C(2)	−566 (5)	1227 (4)	4713 (3)	6.0 (2)
C(3)	−941 (6)	1149 (4)	5321 (3)	7.0 (2)
C(4)	−890 (5)	1741 (5)	5750 (3)	6.7 (2)
C(5)	−396 (5)	2414 (5)	5617 (3)	7.8 (3)
C(6)	49 (5)	2520 (3)	5017 (3)	4.8 (2)
C(7)	−291 (4)	2934 (3)	3552 (2)	3.2 (2)
C(8)	225 (4)	3572 (3)	3340 (2)	3.6 (2)
C(9)	−382 (5)	4208 (3)	3115 (3)	4.7 (2)
C(10)	−1505 (5)	4225 (3)	3134 (3)	4.4 (2)
C(11)	−2042 (5)	3589 (3)	3366 (3)	5.0 (2)
C(12)	−1407 (4)	2933 (3)	3571 (3)	4.3 (2)
C(13)	−50 (4)	1311 (3)	3321 (2)	3.5 (2)
C(14)	275 (5)	555 (3)	3479 (3)	5.1 (2)
C(15)	−44 (5)	−85 (4)	3090 (3)	6.1 (2)
C(16)	−681 (6)	84 (4)	2506 (3)	6.9 (2)
C(17)	−1000 (6)	828 (5)	2339 (3)	7.1 (3)
C(18)	−714 (5)	1445 (3)	2745 (3)	4.7 (2)
C(19)	2432 (4)	3460 (3)	5028 (2)	3.9 (2)
C(20)	2180 (4)	4055 (3)	4588 (3)	4.1 (2)
C(21)	1640 (6)	4705 (4)	4762 (3)	5.9 (2)
C(22)	1368 (6)	4807 (4)	5382 (3)	6.3 (2)
C(23)	1603 (6)	4186 (4)	5817 (3)	5.4 (2)
C(24)	2173 (6)	3531 (3)	5648 (3)	5.3 (2)
C(25)	3074 (5)	1917 (3)	5409 (2)	4.2 (2)
C(26)	3758 (5)	2030 (4)	5998 (3)	5.5 (2)
C(27)	3674 (6)	1521 (4)	6498 (3)	7.0 (3)
C(28)	2937 (7)	908 (4)	6427 (3)	7.8 (3)
C(29)	2288 (6)	763 (4)	5835 (3)	6.8 (2)
C(30)	2380 (5)	1297 (3)	5330 (3)	4.4 (2)
C(31)	4567 (4)	2907 (3)	4848 (2)	4.6 (2)
C(32)	5350 (5)	2299 (5)	4912 (3)	6.4 (2)
C(33)	6474 (6)	2530 (5)	4962 (4)	9.0 (4)
C(34)	6773 (6)	3290 (6)	4924 (4)	9.1 (3)
C(35)	6009 (6)	3871 (5)	4856 (4)	8.5 (3)
C(36)	4872 (5)	3663 (3)	4821 (3)	5.3 (2)
C(37)	3678 (4)	2256 (3)	3177 (2)	3.4 (1)
C(38)	2632 (4)	2016 (3)	2798 (2)	3.5 (2)
C(39)	2085 (5)	2525 (4)	2281 (3)	5.3 (2)
C(40)	4200 (5)	3033 (3)	3089 (3)	4.9 (2)
C(41)	5712 (6)	1553 (4)	2782 (3)	6.7 (2)
C(42)	3534 (7)	33 (4)	3783 (3)	6.7 (2)
C(43)	2547 (7)	775 (4)	1809 (3)	8.1 (3)

[a] Estimated standard deviations in parentheses. [b] Anisotropic thermal parameters in Table IX (supplementary material). [c] The equivalent isotropic thermal parameter is given by $U = {}^1/_3(U_{11} + U_{22} + U_{33} + 2U_{23} \cos \alpha + 2U_{13} \cos \beta + 2U_{12} \cos \gamma)$.

tertiary phosphane ligands, are coupled to ^{195}Pt, with values typical of a tertiary phosphane directly bound to Pt.[16] The doublet and triplet resonances exhibit a phosphorus–phosphorus one-bond coupling, $^1J_{PP}$, only marginally greater in magnitude than the corresponding coupling in the uncomplexed ligand. In addition the striking similarities in the ^{19}F NMR spectra of the free and complexed rings strongly suggest that the bound ring is intact. Only the fluorine atoms of the unique PCF$_3$ unit are coupled to ^{195}Pt, with $^5J_{FPt}$ of 11 Hz. ^{31}P and ^{19}F NMR spectral parameters of I, II, and L are presented in Table III.

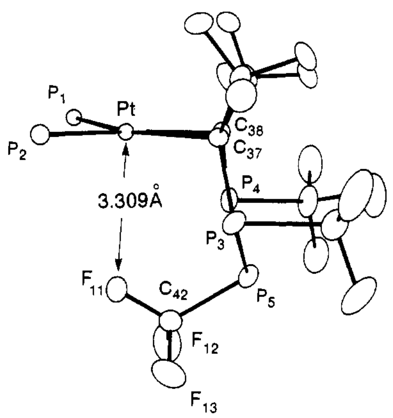
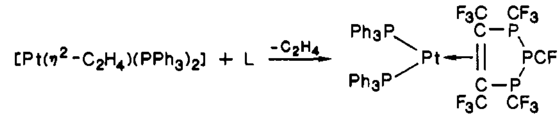


Figure 3. View illustrating the planar character of the P$_3$C$_2$ ring, the orientation of the CF$_3$ groups, and in particular the close approach of the unique CF$_3$ group to the Pt atom.

A single-crystal X-ray structural determination of II showed that the P$_3$C$_2$ ring is indeed intact and furthermore is coordinated to Pt (Figures 1–3) as a normal, if slightly exotic, olefin (eq 3). Final atomic coordinates, selected bond lengths, bond angles, and torsion angles are given in Tables IV–VI.



(3)

The near-planar [PtP$_2$C$_2$] core structure comprising the ring carbons and the Ph$_3$P phosphorus atoms (the dihedral angle between the PtP$_2$ and PtC$_2$ planes is only 3.9°) bears close resemblance to the core structures of other platinum alkene complexes, [Pt(R(R′)C=C(R′)R)(PPh$_3$)$_2$] (R = R′ = Cl,[18] CN;[19] R = H, R′ = CN[20]) (Table VII). In spite of possible extra steric crowding in II, the core structure bears remarkably close similarities to the cores of the di- and tetracyanoethylene complexes.

The polyphosphane heterocycle in compound II is almost perfectly planar (Figures 2 and 3) and subtends an angle of 104.3° to the [PtP$_2$C$_2$] plane (Figure 3). Table VIII contains selected weighted least-squares planes of the molecule. This ring has a small fold about the P(3)–P(4) axis of 5.6°, which is probably a result of balancing the various steric interactions between the CF$_3$ groups on the ring and the interactions between the CF$_3$ group on P(5) and the Pt atom. When the relative rotations of the Ph$_3$P phenyl substituents are disregarded, an approximate mirror plane of symmetry at right angles to the [PtP$_2$C$_2$] plane passes through the metal and the unique phosphorus atom of the ring (P(5)) and bisects the P(2)–Pt–P(1) bond angle. That a true mirror plane exists in the solution state is reflected in the symmetry of the NMR patterns of I and II. The ring retains the *all-trans*-triphospholene configuration postulated by Baudler et al.[21] for rings of this type.

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Table III. NMR[a] Parameters of the Free Ligand (L) and Its Pt(0) Complexes

compd	δ(P)[b]	${}^1J$(P,Pt), Hz	${}^2J$(P,P), Hz	ϕ(F)[c]	${}^2J$(P,F), Hz	${}^3J$(P,F), Hz	J(F,Pt), Hz
I	+2.56[d] (s (br))	3332.0					
	+26.44[e] (d (br))		250.0	−48.60 (d of d (br))	68.5	24.5	
	−13.66[f] (t of m)		250.0	−43.90 (d of t)	68.5	13.0	11.7
				−53.40[g] (m)		26.3[h]	
II	+17.25[d] (s (br))	3518.0					
	+30.27[e] (d (br))		250.0	−49.63 (d of d (br))	65.7	24.1	
	−13.41[f] (t of m)		250.0	−44.40 (d of t)	66.6	11.0	11.5
				−53.34[g] (m)		27.1[h]	
L[i]	+55.0[e] (d)		220	−48.56 (d of d (br))	55	20	
	−41.0[f] (t of m)		220	−46.55 (d of t)	60	20	
				−54.44[g] (m)		27.1[h]	

[a] Recorded in $CDCl_3$ at +25 °C. [b] Relative to 85% H_3PO_4; positive shifts to high frequency (low field) of standard. [c] Relative to $CFCl_3$; negative shifts to low frequency (high field) of standard. Abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. [d] PR_3 resonances. [e] $\{(CF_3)\mathit{P}\}_2PCF_3$ resonances. [f] $\{(CF_3)P\}_2\mathit{P}CF_3$ resonances. [g] CCF_3 resonances—interpreted as X parts of $X_3AA'X'_3$,[17] spin systems complicated by additional coupling to fluorine. ${}^4J$(FF) = 2.4, 2.5, and 4.9 Hz for I, II, and L, respectively. [h] $|{}^3J(PF) + {}^4J(PF)|$ = 26.3, 27.1, and 27.1 Hz for I, II, and L, respectively. [i] Data contained in ref 1.

Table IV. Selected Bond Lengths (Å) in II[a]

Pt–P(1)	2.339 (2)	P(3)–C(37)	1.845 (8)
Pt–P(2)	2.326 (2)	P(4)–C(38)	1.829 (6)
Pt–C(37)	2.092 (6)	C(37)–C(38)	1.490 (9)
Pt–C(38)	2.103 (6)	C(38)–C(39)	1.50 (1)
P(3)–P(5)	2.175 (3)	C(37)–C(40)	1.52 (1)
P(4)–P(5)	2.191 (4)	av P–C[b]	1.824 (13)
P(3)–C(41)	1.92 (1)	av C–F[c]	1.33 (3)
P(4)–C(43)	1.897 (9)	av C–F[d]	1.337 (16)
P(5)–C(42)	1.881 (9)	av C–C[e]	1.40 (2)

[a] Estimated standard deviations in parentheses. [b] P–C bond lengths in Ph_3P ligands. [c] C–F bond lengths in PCF_3. [d] C–F bond lengths in CCF_3. [e] Ph_3P phenyl C–C bond lengths.

Table V. Selected Bond Angles (deg) in II[a]

P(3)–P(5)–P(4)	99.1 (1)	C(37)–P(3)–C(41)	104.7 (4)
P(5)–P(4)–C(38)	100.0 (2)	P(5)–P(3)–C(41)	93.1 (3)
P(5)–P(3)–C(37)	100.6 (3)	P(5)–P(4)–C(43)	92.4 (5)
P(3)–C(37)–C(38)	119.3 (6)	C(38)–P(4)–C(43)	107.4 (4)
P(4)–C(38)–C(37)	120.4 (5)	P(3)–P(5)–C(42)	100.3 (4)
C(37)–Pt–C(38)	41.6 (2)	P(4)–P(5)–C(42)	100.6 (4)
P(1)–Pt–P(2)	103.66 (6)	P(3)–C(37)–C(40)	111.1 (5)
P(1)–Pt–C(38)	106.8 (2)	C(38)–C(37)–C(40)	122.1 (7)
P(2)–Pt–C(37)	107.9 (2)	C(37)–C(38)–C(39)	120.7 (6)
		P(4)–C(38)–C(39)	112.8 (5)

[a] Estimated standard deviations in parentheses.

Table VI. Selected Torsion Angles (deg) in II

C(37)–P(3)–P(5)–P(4)	−3.6
C(38)–P(4)–P(5)–P(3)	6.5
P(5)–P(4)–C(38)–C(37)	−8.9
P(5)–P(3)–C(37)–C(38)	−1.3
P(3)–C(37)–C(38)–P(4)	7.3
C(40)–C(37)–C(38)–C(39)	3.8
C(41)–P(3)–C(37)–C(40)	−55.6
C(43)–P(4)–C(38)–C(39)	48.0
C(43)–P(4)–P(5)–C(42)	−143.0
C(41)–P(3)–P(5)–C(42)	148.2

Consequently, with the metal and the unique CF_3 group on the same face of the ring one of the unique PCF_3 fluorines approaches to within 3.309 Å of the platinum center (Figure 3, F(11)). F(11) lies almost immediately below the metal at a distance that is ca. 0.09 Å greater than the sum of the van der Waals radii[22] (r_w) of F (1.47) and Pt (1.75). A rotation of P(5) to a fully planar position (i.e., ca. 6°) reduces the F···Pt through-space distance to a value smaller (3.19 Å) than the van der Waals distance. Only the fluorines of this unique CF_3 group, which become degenerate in solution probably by rapid rotation about the C(42)–P(5) bond, are coupled to ^{195}Pt, albeit very weakly. It is probable that a "through-space" spin–spin coupling mechanism operates in solution,[23] which may be aided by a small ring-flattening vibration that narrows the F–Pt gap and allows facile van der Waals penetration.[23]

The large shift to low field of the unique PCF_3 phosphorus resonance on coordination is probably related to this coupling mechanism. An alternative possibility for this shift, an induced ring current effect from the triphenylphosphane phenyl substituents, is less probable because an almost identical shift exists for the unique phosphorus in compound I. We conclude that the unique phosphorus in each compound is deshielded by the metal through an agostic[24] Pt–F contact that is fluxional in the solution state (due to rotation about the P(5)–C(42) bond). This contact polarizes the C–F bond further, and in turn the P–C bond, thus drawing electron density from the phosphorus.

The P–P bond lengths in II (2.175 (3), 2.191 (4) Å), while similar to those in 1,2,3-triphenyl-1,2,3-triphosphaindan, $Ph_3P_3C_6H_4$ (2.209 (3) Å),[25] are shorter than in $[(CF_3)P]_4$[26] (2.213 (5) Å), $[(CF_3)P]_5$[27] (mean 2.223 (7) Å), or the diphosphetene $(CF_3)P(CF_3)PC(SiMe_3){=}C(SiMe_3)$[28] (2.223 (1) Å) but are much longer than is typical for diphosphanes[29] (2.004 (6)–2.034 (2) Å). If the strengthening of P–P bonds is not the result of coordination to $[Pt(PPh_3)_2]$, then the P–P bonds in the original ligand must be stronger (shorter) than in other cyclopolyphosphanes, and this may in part explain the lack of ring scission products in this reaction. We note that $[(CF_3)P]_4$,[30] $[(CF_3)P]_5$,[31] and $[(C_6F_5)P]_4$[31] are cleaved by tertiary phosphane complexes of the zerovalent nickel triad metals to give *E*-configuration η^2-(side-bonded)-diorganodiphosphene compounds.[29-31]

The P(3)–P(5)–P(4) bond angle (99.1 (1)°) is similar to the angle in 1,2,3-triphenyl-1,2,3-triphosphaindan (97.3 (1)°)[25] and lies centrally within the ranges found for $[(CF_3)P]_5$ (94.6–107.5° (±0.4°))[27] and for $[PhP]_5$ (94.05 (17)–107.24 (19), mean 100.01 (54)°),[32,33] while it is much less acute than in $[(CF_3)P]_4$ (84.7°).[26] The C–P–P–C torsion angles of the $((CF_3)P)_3$ subunit (143 and 148.2°), while more open than for $[(CF_3)P]_4$ (131.6°),[26] are comparable to the exo C–P–P–C torsion angle in $(F_3C)P(F_3C)PC(SiMe_3){=}C(SiMe_3)$ (148.23°)[28] but tighter than in the complex $[Pd(CF_3P{=}PCF_3)(PPh_3)_2]$ (155.0°),[30] which contains a η^2-diphosphene (P–P bond length 2.121 (2) Å).[30]

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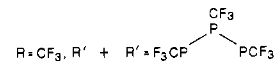
Table VII. Comparison of Structural Details of Selected Platinum Olefin Complexes[a]

	bond lengths, Å					bond angles, deg			
	a	*b*	*c*	*d*	*e*	α	β	γ^b	ref
R = R′ = Cl	2.02 (3)	2.05 (3)	1.62 (3)	2.278 (8)	2.292 (7)	47.1 (2)	100.6 (2)	12.3 (1.5)	18
R = CN, R′ = H	2.025 (6)	2.162 (6)	1.525 (8)	*c*		43 (2)		6	20
R = R′ = CN	2.10 (3)	2.12 (3)	1.49 (5)	2.29 (1) mean		41.5 (1.3)	101.4 (0.3)	8.3	19
	2.103 (6)	2.092 (6)	1.490 (9)	2.339 (2)	2.326 (2)	41.6 (2)	103.66 (6)	3.9	this work

[a] See Figure 5 for the location of the particular lengths and angles compared. [b] γ is the dihedral angle between the weighted least-squares planes [PtP_2] and [PtC_2], where P denotes the tertiary phosphane phosphorus and C the coordinated olefinic carbons. [c] Not available.

Table VIII. Weighted[a] Least-Squares Planes

Definition of Planes

plane	coeff[b]				defining atoms with dev[c]
1	−1.4851	16.6851	−5.0995	1.4579	Pt, P(1), P(2)
2	−2.2376	16.6408	−4.3465	1.5499	Pt, C(37), C(38)
3	−1.5213	−16.7000	4.9942	−1.4926	Pt, 0.001 (0); P(1), −0.007 (1); P(2), −0.008 (1); C(37), −0.128 (6); C(38) −0.076 (5)
4	7.5878	−7.1812	−15.5952	−3.7989	C(37), 0.015 (6); C(38), −0.016 (5); C(39), 0.011 (6); C(40), −0.011 (6)
5	5.6886	2.4074	−19.5734	−3.6253	C(37), 0.042 (5); C(38), 0.131 (5); P(4), −0.021 (2); P(5), 0.027 (2); P(3), −0.019 (2)
6	5.9292	1.3290	−19.5577	−3.6915	C(37), −0.041 (5); C(38), 0.047 (5); P(4), −0.002 (2); P(3), 0.002 (2); *P(5)*, 0.139
7	−5.5545	−2.9490	19.5519	3.6177	P(4), P(5), P(3)

Dihedral Angles[d]

planes	angle	planes	angle	planes	angle	planes	angle
1–2	3.9	1–3	179.7	1–4	107.4	1–5	72.5
1–6	76.2	1–7	109.4	2–3	176.4	2–4	110.8
2–5	75.7	2–6	79.4	2–7	106.2	3–4	72.2
3–5	107.2	3–6	103.4	3–7	70.9	4–5	35.4
4–6	31.7	4–7	142.7	5–6	3.7	5–7	178.1
6–7	174.4						

[a] Weights are derived from the atomic positional esd's by using the method of: Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185. [b] Coefficients are for the form $ax + by + cz - d = 0$, where x, y, and z are crystallographic coordinates. [c] Deviations are in angstroms with the esd's given in parentheses. The atom in italics was not included in the definition of the plane. [d] In degrees.

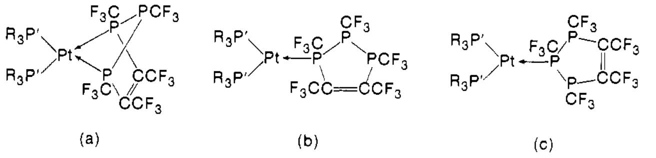


Figure 4. Modes of phosphorus coordination possible for II.

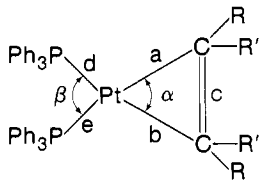


Figure 5. Bond lengths and angles compared in Table VII.

The endo P–C bond lengths in II (1.845 (9) and 1.829 (9) Å) are similar in range to values obtained for three related diphosphetenes, (R)P(R)PC(R′)=C(R′) (R = R′ = Ph, 1.830 (3);[3] R = Ph, R′ = *t*-Bu, 1.847 (4);[3] R = CF_3, R′ = $SiMe_3$, 1.841 (2) Å).[28] These values would seem to indicate very little perturbation of the ring geometry as a result of coordination of the triphospholene olefin functional group. In contrast, the C(37)–C(38) bond length of 1.490 (9) Å, which is similar to that of other Pt–alkene complexes (Table VII), is substantially longer than the mean value of the C=C bond in the three diphosphetenes (1.357 (5) Å),[3,27,32] indicating a considerable reduction in C=C bond order on coordination. However, comparison with the bridging C—C single-bond length in the chelate complex [$PtCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}$][34] (1.538 (14) Å) indicates that the coordinated olefin in II retains some multiple-bond character.

The olefin part of the ring is distorted from planarity on coordination. Thus, the angle between the planes formed by the substituents on the olefin (planes 3 and 5 in Table VIII) is 31.7°. The related angle between the planes of the substituents in [$Pt\{(CN)_2C{=}C(CN)_2\}(PPh_3)_2$] (38.7°)[19] indicates a comparable degree of distortion upon coordination of the olefin to [$Pt(PPh_3)_2$].

Although we do not have any detailed supporting evidence, we suggest that the species responsible for the initial red phases of each reaction may be one or more of several possible phosphane complexes (Figure 4) in which the ring coordinates to the metal through available phosphorus lone pairs. Dimeric complexes containing two [$Pt(PR_3)_2$] moieties bridged by the phosphorus lone pairs of two triphospholenes might be involved, but we think this unlikely in view of the large rings that would be formed in this mode. To date only a cyclotriphosphane has shown such bimetallic bridging complexation.[35]

The olefin–metal complex formed herein is undoubtedly a reflection of the balance of σ-donor and π-acceptor abilities of each type of coordination site in L. Perfluoromethyl–phosphorus ligands are known to be weak σ donors but strong π acids.[36] Clearly the much stronger π acidity of the olefin in L, which appears comparable to that of tetracyanoethylene, has favored this binding site over σ-bond formation between Pt and phosphorus.

It seems reasonable to suspect that the more open face of the triphospholene is coordinated to platinum because the two CF_3 substituents on phosphorus α to the olefin either acted as a steric disincentive to coordination of that flank or hindered the approach of the zerovalent metal moiety.

The structural similarity of L and TCNE complexes of Pt(0) suggests a similar π acidity for both ligands. It is therefore curious that L does not complex with Vaska's compound[28] whereas TCNE does so readily.[37] We suspect that the reason is steric. In order

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to maintain the all-trans planar geometry of the coordinated ring of L, the CF_3 group of the phosphorus atom at the apex must sit over the metal as it does in the structure of II. The crystal structure of the complex *cis*-$[IrBr(CO)\{C(CN)_2{=}C(CN)_2\}(PPh_3)_2]$[19] shows that the sites above and below the M-(TCNE)$(PPh_3)_2$ plane are blocked by CO and Br ligands, so that the CF_3 group of the ligand L cannot be accommodated without distorting the framework. The lack of complex formation with Vaska's compound suggests also that this phospholene ligand may not be readily deformed from the all-trans planar geometry exhibited by II.

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Registry No. I, 110718-07-5; II, 110718-08-6; L, 2546-25-0; $[Pt(PEt_3)_4]$, 33937-26-7; $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$, 12120-15-9.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table IX), rms thermal vibrations (Table X), all bond distances (Table XI), all bond angles (Table XII), and torsional angles (Table XIII) (9 pages); a listing of calculated and observed structure factors (Table XIV) (54 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
State University of New York at Albany, Albany, New York 12222

Derivatized Polyoxomolybdates. Synthesis and Characterization of Oxomolybdate Clusters Containing Coordinatively Bound Diazenido Units. Crystal and Molecular Structure of the Octanuclear Oxomolybdate $(NHEt_3)_2(n\text{-}Bu_4N)_2[Mo_8O_{20}(NNPh)_6]$ and Comparison to the Structures of the Parent Oxomolybdate α-$(n\text{-}Bu_4N)_4[Mo_8O_{26}]$ and the Tetranuclear (Diazenido)oxomolybdates $(n\text{-}Bu_4N)_2[Mo_4O_{10}(OMe)_2(NNPh)_2]$ and $(n\text{-}Bu_4N)_2[Mo_4O_8(OMe)_2(NNC_6H_4NO_2)_4]$

Tze-Chen Hsieh, Shahid N. Shaikh, and Jon Zubieta*

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Reactions of α-$(n\text{-}Bu_4N)_4[Mo_8O_{26}]$ with phenylhydrazine yield a variety of derivatized polyoxomolybdates containing the *cis*-bis(diazenido)molybdenum core $[Mo(NNPh)_2]^{2+}$. When the reaction is carried out in methanol with excess (*p*-nitrophenyl)hydrazine, $(n\text{-}Bu_4N)_2[Mo_4O_8(OMe)_2(NNAr)_4]$ is the major product. The tetranuclear polyoxomolybdate unit consists of the $[Mo_2(\mu\text{-}OMe)_2(NNAr)_4]^{2+}$ core, bridged by two doubly bridging bidentate $[MoO_4]^{2-}$ moieties. On the other hand, when the molybdate is present in excess, the unsymmetrically substituted tetranuclear cluster $(n\text{-}Bu_4N)_2[Mo_4O_{10}(OMe)_2(NNPh)_2]$ is isolated. This species is structurally analogous to $[Mo_4O_8(OMe)_2(NNPh)_4]^{2-}$, presenting the $[Mo_2O_2(\mu\text{-}OMe)_2(NNPh)_2]^{2+}$ core, and is characterized by a *cis*-$[MoO_2]^{2+}$ unit and a single *cis*-$[Mo(NNPh)_2]^{2+}$ unit, bridged by two methoxy groups. The tetranuclear unit is completed by the doubly bridging $[MoO_4]^{2-}$ units. In contrast, reactions of phenylhydrazine and NEt_3 with α-$(n\text{-}Bu_4N)_4[Mo_8O_{26}]$ in acetonitrile yield the octanuclear polyoxomolybdate $(NHEt_3)_2(n\text{-}Bu_4N)_2[Mo_8O_{20}(NNPh)_6]$. The structure is related to that of the α-$[Mo_8O_{26}]^{4-}$ parent polyoxomolybdate, by substitution of the two terminal oxo groups on each of three alternate molybdenum centers in the Mo_6O_6 crown and rotation of the pole-capping $[MoO_4]^{2-}$ units by ca. 45°, so as to engage three doubly bridging Mo_2O interactions per unit rather than three triply bridging Mo_3O interactions. The ^{17}O NMR spectra of the derivatized species are consistent with the solid-state structures, exhibiting resonances in the regions assigned to doubly bridging Mo_2O groups (400–520 ppm) and to terminal MoO groups (700–950 ppm). Crystal data are as follows. α-$(n\text{-}Bu_4N)_4[Mo_8O_{26}]$: monoclinic space group $P2_1/n$, with $a = 15.093$ (3) Å, $b = 16.011$ (3) Å, $c = 18.519$ (4) Å, $\beta = 91.36$ (1)°, $V = 4473.9$ (3) Å^3, and $Z = 2$. Structure solution based on 3274 reflections converged at $R = 0.039$. $(n\text{-}Bu_4N)_2[Mo_4O_8(OMe)_2(NNC_6H_4\text{-}p\text{-}NO_2)_4]$: monoclinic space group $P2_1/n$, with $a = 15.723$ (2) Å, $b = 14.058$ (2) Å, $c = 16.607$ (3) Å, $\beta = 95.28$ (1)°, $V = 3655.1$ (2) Å^3, and $Z = 2$. Structure solution and refinement based on 2988 reflections converged at $R = 0.063$. $(n\text{-}Bu_4N)_2[Mo_4O_{10}(OMe)_2(NNPh)_2]$: monoclinic space group $C2/c$, with $a = 15.472$ (2) Å, $b = 20.516$ (3) Å, $c = 19.077$ (2) Å, $\beta = 91.23$ (1)°, $V = 6054.1$ (2), and $Z = 4$. Structure solution and refinement based on 1670 reflections converged at $R = 0.066$. $(NHEt_3)_2(n\text{-}Bu_4N)_2[Mo_8O_{20}(NNPh)_6]$: $P2_1/c$ with $a = 18.495$ (3) Å, $b = 26.783$ (5) Å, $c = 21.470$ (4) Å, $\beta = 95.57$ (1)°, $V = 10585.0$ (9) Å^3, and $Z = 4$; 6525 reflections, $R = 0.051$.

The polyoxoanions of molybdenum and tungsten have attracted continuing interest as catalysts, as spectroanalytical reagents, as imaging agents for electron microscopy, and as catalysts in the photooxidation of organic compounds.[1,2] Although the perceived analogies of the isopolymolybdate anions to metal oxide surfaces provide a current focus of attention, relatively few examples of organic derivatives of isopolymolybdates have been reported.[3-6] The coordination chemistry of the isopolymolybdates had been limited to the formylated derivative $[(HCO)_2Mo_8O_{28}]^{6-}$, the methoxy derivative $[Mo_8O_{24}(OCH_3)_4]^{4-}$, species formally incorporating an acetal group $[CH_2Mo_4O_{15}H]^{3-}$ and the related formylated methylenedioxomolybdate–formate cluster $[HCCHMo_4O_{17}CH]^{3-}$, and the pyridine-coordinated complex $[(C_5H_5N)_2Mo_8O_{26}]^{4-}$.[3-6] In each of these examples, the molybdenum centers are pseudooctahedrally coordinated either to six oxygen donors or, in the case of the pyridine-coordinated centers of $[(C_5H_5N)_2Mo_8O_{26}]^{4-}$, to five oxygen donors and a single pyridyl nitrogen.

We have recently demonstrated that the derivative chemistry of the isopolymolybdates may be extended to the organodiazenido group, –NNR,[7-9] and to the organohydrazido unit, –NNRR′,[10]

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