(3) Å, b = 10.330 (2) Å, c = 14.300 (4) Å, β = 112.05 (1)°, V = 1335.0 Å^3, Z = 4, d_{calcd} = 2.092 g cm^{-3}, with space group $P2_1/c$.

A total of 3523 reflections were collected with use of standard moving-crystal moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0 + dispersion, single background time at extremes of scan = 4 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were 5° < 2θ < 50°. The number of reflections with F > 2.33σ_F was 2758. The data were corrected for absorption: the linear absorption coefficient was 87.135 cm^{-1} with minimum and maximum corrections of 0.152 and 0.311, respectively.

The structure was solved by direct methods and refined with use of full-matrix techniques, including all hydrogen atoms, to give final residuals R_F = 0.038 and R_{wF} = 0.040. The goodness of fit for the last cycle was 1.057, and the maximum Δ/σ was 0.05.

[TaCl$_2$(NMe$_2$)$_2$(HNMe$_2$)]$_2$O. A yellow crystal of dimensions 0.14 × 0.16 × 0.24 mm was examined. The orange crystals selected at ambient temperatures all exhibited reversible chromic behavior, turning yellow upon cooling to −171 °C. The cell dimensions obtained from 29 reflections at −171 °C with Mo Kα (λ 0.71069 Å) were a = 8.314 (1) Å, b 20.480 (4) Å, c = 15.778 (3) Å, β = 112.22 (1)°, V = 1243.6 Å^3, Z = 4, d_{calcd} = 2.241 g cm^{-3}, with space group $P2_1/c$.

A total number of 11 996 reflections were collected with use of standard moving-crystal moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0 + dispersion, single background time at extremes of scan = 5 s, aperture size = 3.0 ×

4.0 mm. The limits of data collection were 5° < 2θ < 50°. Of 5718 unique intensities, the number of reflections with F > 2.33σ_F was 5064. The data were corrected for absorption: the linear absorption coefficient was 91.390 cm^{-1} with minimum and maximum corrections of 0.195 and 0.377, respectively.

The structure was solved by direct methods and refined by full-matrix techniques, including hydrogen atoms with fixed thermal parameters, to give final residuals R_F = 0.047 and R_{wF} = 0.044. The goodness of fit for the last cycle was 1.155, and the maximum Δ/σ was 0.05.

Registry No. [TaCl$_2$(NMe$_2$)$_3$]$_2$, 77071-68-2; TaCl$_3$(NMe$_2$)$_2$-(HNMe$_2$), 77071-69-3; [TaCl$_2$(NMe$_2$)$_2$(HNMe$_2$)]$_2$O, 77071-70-6; TaCl$_2$(NMe$_2$)$_3$(HNMe$_2$), 77071-71-7; Me$_2$NH$_2$$^+Cl^-$, 506-59-2; Ta-(NMe$_2$)$_5$, 19824-59-0; Me$_3$SiCl, 75-77-4; TaCl$_5$, 7721-01-9.

Supplementary Material Available: Tables of observed and calculated structure factors (98 pages). Ordering information is given on any current masthead page. The complete structural reports, MSC Reports 7941, 8004, and 8007, are available upon request, in microfiche form only, from the Indiana University Library.

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The μ-Oxo-decachloroditantalum(V) Ion

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The compound [P(CH$_3$)$_3$C$_6$H$_5$]$_2$[Ta$_2$Cl$_{10}$O] was prepared serendipitously and the structure determined by X-ray crystallography. The compound crystallizes in space group $P2_1/c$ with Z = 2. The unit cell dimensions are a = 8.479 (3) Å, b = 19.577 (5) Å, c = 10.285 (4) Å, and β = 103.87 (8)°. The [Ta$_2$Cl$_{10}$O]$^{2-}$ ion has a crystallographic inversion center but approximates very closely to D_{4h} (4/*mmm*) symmetry. The important bond lengths and angles are as follows: Ta–O, 1.880 (1) Å; Ta–Cl(trans), 2.381 (6) Å; average Ta–Cl(cis), 2.336 ± 0.004 Å; average O–Ta–Cl(cis), 90.9 ± 0.5°. This is the first species of its kind lacking metal d electrons, and comparisons are made with structurally similar species of W, Re, Ru, and Os with 4–8 metal d electrons.

Introduction

Linear oxo bridges, X–O–X, have long been of interest with respect to the problem of correlating their linearity with the character of the X–O bonds. Simple σ bonds, as in H$_2$O, ethers, etc., are in general best formed by using two orbitals of mainly 2p character, leaving one lone pair in a very low-energy orbital of mainly 2s character and the other lone pair in an orbital of nearly pure 2p character that has a node in the plane defined by the bent, symmetrical X–O–X triad. In some cases the X–O–X angle becomes quite large, allegedly because of increased π contributions to the X–O bonds. In the limit of a linear X–O–X triad, the opportunity for X–O π bonding is maximal and also governed by symmetry restrictions in a way that is helpful in discussing the pertinent orbital overlaps.

The most intensively studied examples of linear X–O–X containing systems are those anions in which X is a Cl$_5$M moiety, where M is a transition metal. These anions have D_{4h} symmetry, which makes qualitative analysis of the bridge bonding simple and convenient. The first such anion to be characterized structurally[1] and analyzed theoretically[2] was

[Cl$_5$RuORuCl$_5$]$^{4-}$. The accuracy of the structure determination of this anion has since been increased.[3] In addition, the four ions containing W^{IV}W^{IV}, Re^{IV}Re^{IV}, Re^{IV}Re^V, and Os^{IV}Os^{IV} have been discovered and extensively studied by X-ray crystallography,[4-7] spectroscopy,[8-12] and magnetic measurements.[13] Actually, [Cl$_5$ReOReCl$_5$]$^{4-}$ was the first

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Table I. Crystallographic Parameters for [PMe₃Ph] [Ta₂Cl₁₀O]

space group	$P2_1/c$
a, Å	8.479 (3)
b, Å	19.577 (5)
c, Å	10.285 (4)
β, deg	103.87 (8)
V, Å³	1657 (2)
d_{calcd}, g/cm³	1.756
Z	2
fw	876.58
cryst size, mm	0.1 × 0.2 × 0.5
μ(Mo Kα), cm⁻¹	78.022
range 2θ, deg	0-50
no. unique data	1516
no. data, $F_o^2 > 3\sigma(F_o^2)$	1139
no. variables	152
R_1	0.056
R_2	0.059
goodness of fit	1.357
largest shift[a]	0.56 × esd
largest shift,[b] e/Å³	0.745

[a] Largest parameter shift in final least-squares calculation.
[b] Largest peak in the final difference fourier map.

to be reported, having been discovered by Noddack and Noddack in 1933.[14]

All of these previously known [Cl₅MOMCl₅]ⁿ⁻ ions contain metal ions that possess d electrons: two for W^{IV} and Re^{V}, three for Re^{IV}, and four for Ru^{IV} and Os^{IV}. Discussions of the M–O–M bonding have considered how these metal d electrons, along with the two pairs of π electrons on the bridging oxygen atom, would occupy the π and δ MO's, how the M–O bond orders would thus be determined, and how the M–O bond lengths, force constants, and stretching frequencies as well as the electronic spectra and magnetic properties of the M–O–M unit would be influenced.

With respect to the understanding of these M–O–M units, it is clearly of value to have the type in which there are no metal d electrons available as a limiting case. We report here the preparation and structural characterization of the first anion of this type, [Cl₅TaOTaCl₅]²⁻.

Experimental Section

All materials were handled under argon with use of Schlenk or vacuum line techniques. Solvents were distilled over sodium benzophenone ketyl under argon. Tantalum pentachloride (99+%) was purchased from the Alfa Division of Ventron Corp. Dimethylphenylphosphine, PMe₂Ph, was purchased from Strem Chemicals, Inc.

Preparation. Dimethylphenylphosphine, PMe₂Ph (3.00 g, 21.7 mmol), was added to a suspension of TaCl₅ (1.94 g, 5.4 mmol) in toluene (30 mL) at room temperature. Two equivalents of sodium amalgam (0.2%) was added to the stirred mixture. The initial yellow suspension gave a dark green solution after intermittent shaking over a 2-h period. The solution was filtered and allowed to stand 24 h. Oxygen was admitted to the flask, and a yellow-brown solution with yellow crystals was obtained upon standing 8 h.

X-ray Crystallography. Collection of Data. Crystals suitable for data collection were sealed in capillaries under nitrogen. Data were collected on an Enraf-Nonius CAD-4F diffractometer at 26 ± 1 °C using Mo Kα radiation (λ = 0.710 73 Å) with a graphite-crystal monochromator in the incident beam. Other details concerning collection and processing of data have appeared before.[15] The usual Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on ψ scans of nine reflections at χ = 90° was also applied. Crystallographic parameters and a summary of data collection and refinement parameters are presented in Table I.

The intensities of three standard reflections were measured every 30 min of X-ray exposure; each showed a total decrease in intensity
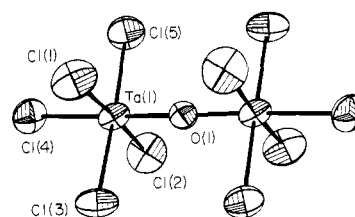
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Figure 1. [Ta₂Cl₁₀O]²⁻ ion showing the thermal ellipsoids of the atoms and the atom labeling scheme. The O(1) atom residues on an inversion center.
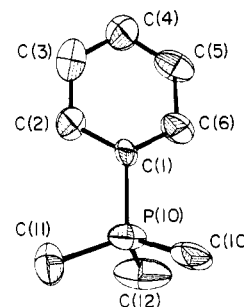

Figure 2. [P(CH₃)₃C₆H₅]⁻ ion showing the atom labeling scheme.

of about 22%, but the decay rates were not identical. A correction for anisotropic decay was therefore applied to the data. This correction factor was obtained by interpolating between the two nearest (in terms of time) standard reflections, after having corrected those standards to zero time. The contribution of each standard toward determining the correction factor for a given reflection is weighted to account for the relative distance between reciprocal lattice points. The program CHORTA-1, which is part of the standard CAD-4 software, was used for this purpose.

Structure Solution. Data were collected for a monoclinic system. The observed volume was consistent with Z = 2. Inspection of the data revealed systematic absences for $h0l$, l = 2n, and $0k0$, k = 2n, which uniquely determine the space group as $P2_1/c$. The position of the tantalum atom was determined from a three-dimensional Patterson function and refined by the full-matrix least-squares method. Subsequent difference Fourier maps followed by least-squares refinement located all nonhydrogen atoms. Anisotropic thermal parameters were assigned to the nonhydrogen atoms, and the structure refined to final discrepancy factors of

$$R_1 = \sum ||F_o| - |F_c||/\sum |F_o| = 0.056$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.059$$

The final difference map showed no peaks of structural significance. A table of structure factors is available as supplementary material.

Results

The positional and thermal parameters for all of the nonhydrogen atoms are listed in Table II. The cations [P(CH₃)₃C₆H₅]⁺ reside on general positions, while the anions [Cl₅TaOTaCl₅]²⁻ are located on positions of crystallographic inversion symmetry. The Ta–O–Ta unit is thus constrained to be linear (barring disorder, for which there is no evidence), and the two TaCl₅ moieties are crystallographically equivalent. The [Cl₅TaOTaCl₅]²⁻ ion is depicted and the numbering scheme defined in Figure 1. The same information is given for the [P(CH₃)₃(C₆H₅)]⁺ ion in Figure 2. Table III gives the bond lengths and angles in the anion and Table IV those in the cation.

Within the errors, the dimensions of the [P(CH₃)₃(C₆H₅)]⁺ ion are normal and require no comment.

The dimensions of the [Cl₅TaOTaCl₅]²⁻ ion conform within the uncertainties to D_{4h} symmetry. They will be compared with those of the other [Cl₅MOMCl₅]ⁿ⁻ ions in the Discussion.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Ta(1)	0.0408 (1)	0.07874 (6)	0.1075 (1)	3.85 (4)	4.11 (4)	2.96 (3)	0.07 (7)	1.57 (3)	0.21 (6)
Cl(1)	0.3166 (8)	0.0742 (5)	0.1090 (7)	3.1 (3)	9.3 (5)	7.5 (4)	0.8 (4)	1.2 (3)	0.1 (4)
Cl(2)	−0.2359 (7)	0.0887 (4)	0.1006 (7)	4.2 (3)	7.8 (5)	7.2 (3)	0.5 (4)	3.4 (2)	−0.6 (4)
Cl(3)	−0.0010 (9)	0.1497 (4)	−0.0810 (6)	7.2 (4)	7.1 (4)	4.5 (3)	1.4 (4)	2.8 (3)	1.1 (3)
Cl(4)	0.0952 (9)	0.1769 (4)	0.2477 (7)	7.9 (4)	5.5 (4)	4.2 (3)	−0.9 (4)	1.6 (3)	−1.0 (3)
Cl(5)	0.0850 (10)	0.0116 (4)	0.2995 (6)	10.7 (5)	5.9 (4)	3.8 (3)	−0.5 (4)	1.6 (3)	0.8 (3)
P(10)	0.3753 (9)	0.3625 (4)	0.1974 (7)	2.2 (8)	5 (1)	5.2 (9)	0.1 (9)	2.4 (7)	1 (1)
O(1)	0.0000 (0)	0.0000 (0)	0.0000 (0)	4.8 (3)	5.6 (4)	4.7 (3)	−0.1 (3)	2.3 (3)	−1.4 (3)
C(1)	0.521 (3)	0.345 (1)	0.094 (2)	2 (1)	5 (1)	1.9 (8)	0 (1)	−0.3 (8)	−0 (1)
C(2)	0.501 (3)	0.380 (1)	−0.023 (2)	7 (1)	7 (2)	4 (1)	1 (1)	3 (1)	2 (1)
C(3)	0.623 (3)	0.369 (2)	−0.100 (2)	7 (1)	7 (2)	5 (1)	−1 (1)	4 (1)	0 (1)
C(4)	0.749 (3)	0.324 (2)	−0.055 (3)	5 (1)	8 (2)	5 (1)	1 (1)	1 (1)	0 (1)
C(5)	0.755 (4)	0.290 (1)	0.066 (3)	6 (2)	7 (2)	6 (2)	2 (2)	0 (1)	2 (1)
C(6)	0.643 (3)	0.303 (1)	0.147 (2)	2 (1)	6 (1)	4 (1)	−1 (1)	0.2 (9)	0 (1)
C(10)	0.170 (3)	0.346 (2)	0.101 (2)	5 (1)	10 (2)	4 (1)	−0 (1)	3.3 (9)	0 (1)
C(11)	0.416 (3)	0.308 (2)	0.348 (3)	6 (2)	8 (2)	5 (1)	1 (1)	−0 (1)	1 (1)
C(12)	0.388 (4)	0.449 (2)	0.242 (3)	13 (2)	6 (2)	11 (2)	−1 (2)	8 (1)	−2 (1)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$, where a, b, and c are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Bond Lengths and Angles in the $[Cl_5TaOTaCl_5]^{2-}$ Ion

A. Bond Lengths, Å

Ta–O	1.880 (1)	Ta–Cl(5)	2.327 (6)
Ta–Cl(1)	2.336 (6)	av Ta–Cl(cis)	2.336 ± 0.004
Ta–Cl(2)	2.339 (6)	Ta–Cl(4)	2.381 (6)
Ta–Cl(3)	2.341 (6)		

B. Bond Angles, Deg

O–Ta–Cl(1)	90.9 (2)	Cl(4)–Ta–Cl(1)	88.8 (3)
O–Ta–Cl(2)	90.5 (2)	Cl(4)–Ta–Cl(2)	89.8 (2)
O–Ta–Cl(3)	91.7 (2)	Cl(4)–Ta–Cl(3)	89.5 (3)
O–Ta–Cl(5)	90.3 (2)	Cl(4)–Ta–Cl(5)	88.4 (3)
av O–Ta–Cl(cis)	90.9 ± 0.5	av Cl(trans)–Ta–Cl(cis)	89.1 ± 0.5
O–Ta–Cl(4)	178.7 (2)	Cl(1)–Ta–Cl(2)	177.1 (3)
		Cl(3)–Ta–Cl(5)	178.0 (2)

Table IV. Bond Lengths and Angles in the $[P(CH_3)_3C_6H_5]^+$ Ion

A. Bond Lengths, Å

P–C(10)	1.81 (3)	C(1)–C(2)	1.35 (3)
P–C(11)	1.85 (3)	C(2)–C(3)	1.46 (3)
P–C(12)	1.75 (3)	C(3)–C(4)	1.38 (3)
av P–CH₃	1.80 ± 0.04	C(4)–C(5)	1.41 (4)
P–C(1)	1.85 (2)	C(5)–C(6)	1.42 (4)
		C(6)–C(1)	1.34 (3)
		av ring C–C	1.39 ± 0.04

B. Bond Angles, Deg

C(1)–P–C(10)	110 (1)	C(11)–P–C(12)	111 (1)
C(1)–P–C(11)	111 (1)	min ring C–C–C	115 (2)
C(1)–P–C(12)	109 (1)	max ring C–C–C	127 (2)
C(10)–P–C(11)	108 (1)	av ring C–C–C	120 ± 4
C(10)–P–C(12)	108 (2)		

Table V. Bond Lengths (Å) in Known Structures of $[M_2Cl_{10}O]^{n-}$ Ions

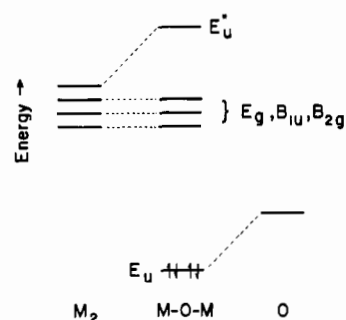| M	n	d electrons per M	total	M–O	M–Cl(cis)	M–Cl-(trans)	ref
Ta[V]	2	0	4	1.880 (1)	2.336 (4)	2.381 (6)	
W[IV]	4	2	8	1.871 (1)	2.410 (2)	2.406 (5)	4
Re[IV,V]	3	2¹/₂	9	1.832 (2)	2.349 (4)	2.379 (7)	6
Re[IV]	4	3	10	1.865 (2)	2.385 (3)	2.397 (11)	5
Os[IV]	4	4	12	1.778 (2)	2.371 (2)	2.433 (7)	7
Ru[IV]	4	4	12	1.801 (2)	2.362 (2)	2.317 (7)	3

Figure 3. Qualitative energy level diagram for the non σ orbitals of an M–O–M group. The presence of only four electrons, as is the case for Ta[V]–O–Ta[V], is indicated.

Discussion

The compound we are reporting here makes the sixth $[Cl_5MOMCl_5]^{n-}$ ion whose structure has been determined. Pertinent data for all of these structures are collected in Table V.

The M–O–M bonding scheme first proposed by Dunitz and Orgel[2] has been accepted by all subsequent investigators, and there is no doubt that it is qualitatively correct. It is derived by considering only the interactions among eight orbitals, namely, three d orbitals (two of π character and one δ) on each metal atom and two $p\pi$ orbitals on the oxygen atom; it leads to the picture shown in Figure 3. We show here the presence of only four electrons in the bonding E_u orbital; these four electrons originate with the oxygen atom and are an invariant part of the scheme. Additional electrons that may be brought in by the metal atoms will have to occupy the central set of

orbitals that are, to a first approximation, nonbonding. It should also be mentioned that the exact ordering of this group of nonbonding orbitals cannot be predicted easily. It may well vary from one of the species in Table V to another.

From all of the results in Table V, it seems that the central orbitals are all essentially nonbonding, but perhaps not precisely so. Detailed analysis is not possible because we do not know for certain the order of these levels. However, the following observations suggest that at least some of these orbitals may be slightly bonding in character. On going from Ta[V]–O–Ta[V] to W[IV]–O–W[IV], we might expect a slight increase in the metal radius because of the lower degree of ionization. This should lead to a slight lengthening of the M–Cl bonds and to an equal or greater lengthening of the M–O bonds because, in addition to the increase in metal atom radius, there is a lesser tendency for the initially oxygen $p\pi$ electrons to be drawn toward the metal atoms. There is, in fact, a lengthening of the W–Cl bonds compared to the Ta–Cl bonds, by about 0.07 Å for the cis ones and about 0.025 Å for the trans ones,

but the W–O bonds are about 0.01 Å shorter than the Ta–O bonds. Thus, the first four electrons entering the central set of "nonbonding" orbitals enter an orbital or orbitals that are slightly bonding in character. The same general trend can be seen with the last two electrons that can enter these orbitals by comparing the bond lengths in the $[Cl_3ReOReCl_5]^{4-}$ and $[Cl_5OsOOsCl_5]^{4-}$ ions. Although the M–Cl bonds increase slightly in length, the M–O bonds become shorter by ca. 0.08 Å. The ninth and tenth total electrons may well be entering a truly nonbonding orbital, since from $[Cl_5WOWCl_5]^{4-}$ to $[Cl_5ReOReCl_5]^{4-}$ there are similar slight decreases in both the M–Cl distances and the M–O distances. The change from 9 total electrons to 10 when represented by the reduction of $[Cl_5ReOReCl_5]^{3-}$ to $[Cl_5ReOReCl_5]^{4-}$ leads to a uniform decrease of about 0.03 Å in all Re–Cl and Re–O bond lengths, which may be understood by assuming that the electron is entering an essentially nonbonding orbital but that the lowering of the mean oxidation number increases the covalent radius by about 0.03 Å.

Finally, we note that this $[Cl_5TaOTaCl_5]^{2-}$ ion must share the honor of being the first $Ta^V–O–Ta^V$ species to be reported with a compound described in the preceding paper by Chisholm, Huffman, and Tan,[16] namely, $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$. That molecule has also been structurally

characterized by X-ray crystallography. It lies on a general position in the unit cell, and therefore linearity of the Ta–O–Ta group is not required. However, it is only slightly bent (174°), and the two Ta–O bond lengths are practically equal at 1.928 (6) and 1.917 (6) Å. The average, 1.922 (5) Å, is significantly longer than the Ta–O distance in $[Cl_5TaOTaCl_5]^{2-}$, 1.880 (1) Å. Another interesting difference is in the lengths of the cis and trans Ta–Cl bonds. In $[Cl_5TaOTaCl_5]^{2-}$ the trans bond is longer by 0.045 (7) Å than the cis one, whereas in Chisholm's compound the trans bonds are shorter, by about 0.10 ± 0.01 Å, than the cis bond. Both of these differences can be understood as arising from the strong tendency of the NMe_2 groups to engage in donor π bonding to the metal atoms. This tendency is greater for the NMe_2 groups than for the bridging oxygen atoms, and thus the Ta–O bonds have less π character and are longer in Chisholm's compound than in ours. Furthermore, the trans influence of the NMe_2 group is then greater than that of the oxygen atom, thus causing the cis Cl atom, which is trans to an NMe_2 group, to have a longer bond than the trans Cl atom.

(16) Chisholm, M. H.; Huffman, J. C.; Tan, L.-S. *Inorg. Chem.*, preceding paper in this issue.

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Further Studies of the Unusual Nature of Tris(β-cyanoethyl)phosphine: Structures of the Phosphine and the Phosphine Oxide

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The crystal and molecular structures of tris(β-cyanoethyl)phosphine (1) and the phosphine oxide (2) have been determined. The structure of the phosphine (1) was solved and refined in space group $P2_1/m$ with $a = 6.812$ (3) Å, $b = 12.988$ (7) Å, $c = 5.869$ (2) Å, $\beta = 91.08$ (3)°, and $Z = 2$. The molecules lie in mirror planes and are significantly distorted from threefold symmetry. The C–P–C angles are 106.9 (1) (twice) and 97.1 (2)° while the other dimensions that should be chemically equivalent also show discrepancies, e.g., P–C = 1.818 (5) (twice) and 1.841 (2) Å and C–N = 1.156 (3) (twice) and 1.111 (6) Å. The distortions as well as the high melting point of the phosphine are attributed to intermolecular dipole–dipole forces. The oxide (2) crystallizes in the hexagonal space group $R3c$ with $a = 13.487$ (3) Å, $c = 10.166$ (1) Å, and $Z = 6$. The structure refined smoothly to $R_1 = 0.028$ and $R_2 = 0.037$. The molecule has crystallographic 3 symmetry with P–O = 1.498 (3) Å, P–C = 1.803 (2) Å, C–C = 1.519 (3) Å, C–CN = 1.459 (3) Å, C≡N = 1.133 (3) Å, O–C–C = 112.04 (8)°, and C–P–C = 106.78 (9)°.

Introduction

For many years the unusual character of tris(β-cyanoethyl)phosphine, $P(CH_2CH_3CN)_3$ (1), has been recognized. Most immediately obvious, perhaps, is its stability toward oxidation by O_2, which is in sharp contrast to the easy conversion of typical trialkylphosphines to the phosphine oxides. Tris(β-cyanoethyl)phosphine, on the contrary, resembles triarylphosphines such as $P(C_6H_5)_3$ in requiring the use of stronger oxidizing reagents. It was also shown 20 years ago that it has very low basicity, more like that of $P(C_6H_5)_3$ than $P(C_2H_5)_3$, as shown by its HNP value of 679 relative to 573 for $P(C_6H_5)_3$ and 111 for $P(C_2H_5)_3$.[2] [ΔHNP stands for

change in the half-neutralization potential in a type of nonaqueous titration, and ΔHNP values are an inverse measure of Lewis basicity. See ref 2 for further details.] It is also the only phosphine yet known to react with $Ni(CO)_4$ to produce a metal atom cluster compound, viz., $Ni_4(\mu\text{-}CO)_6[P(CH_2CH_2CN)_3]_4$.[3]

Spectroscopic and structural data for $(NCCH_2CH_2)_3PM(CO)_n$ complexes have recently become available and serve to broaden the base of evidence for its unusual place among the phosphines. Measurements of ν_{CO}[4,6] and ^{13}C NMR

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