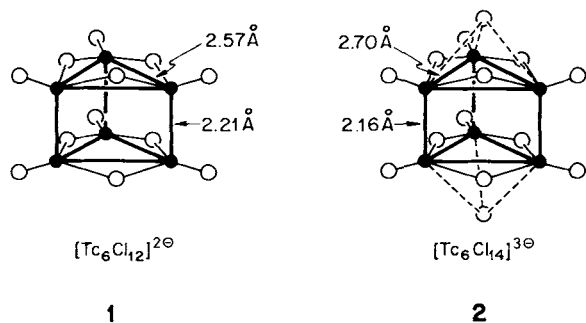


- [6] Light sources: Osram HBO 200-W high-pressure mercury lamp equipped with Bausch & Lomb monochromator (halfwidth 10 nm); Gränztel low-pressure mercury lamp (spiral lamp, 150 W). Cooling apparatus: Displex Closed Cycle Refrigeration System 202 (Air Products).
- [7] The reaction of $^3\text{CH}_2$ with nitrogen upon irradiation of diazomethane **3** in a N_2 matrix was first suggested by Pimentel et al. [3b] on the basis of labeling experiments. The formation of **3** from **1a** via **2a** confirms the required type of reaction. This also explains why **3** and diazirine (which is converted into **3** before undergoing elimination of N_2 upon irradiation in a matrix) are very poor precursors for methylene in matrix isolation experiments. Under these conditions, **3** is apparently "photostable" for a long period of time because the N_2 formed is immediately trapped again by CH_2 .
- [8] D. W. Smith, L. Andrews, *J. Chem. Phys.* 58 (1973) 5222.
- [9] The position found by us differs considerably from that for the $^{\ominus}\text{CH}_2\text{Cl}$ cation (1040 cm^{-1}) derived from the PE spectra: L. Andrews, J. M. Dyke, N. Jonathan, N. Keddar, A. Morris, *J. Am. Chem. Soc.* 106 (1984) 299.
- [10] We thank Dr. B. P. Winnewisser, Universität Giessen, for this calculation.
- [11] H. Siebert: *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*. Springer, Berlin 1966.
- [12] Bands of the kind discussed here were observed previously in photolysis [G. P. Brown, J. P. Simons, *Trans. Faraday Soc.* 65 (1969) 3245; H. Mohan, K. N. Rao, R. M. Fyer, *Radiat. Phys. Chem.* 23 (1984) 505] and radiolysis of dihalomethanes [L. Andrews, F. T. Prochaska, B. S. Ault, *J. Am. Chem. Soc.* 101 (1978) 9], but were assigned to other species.
- [13] a) R. Weiss, H. Wolf, U. Schubert, T. Clark, *J. Am. Chem. Soc.* 103 (1981) 6142; b) A. E. Reed, F. Weinhold, R. Weiss, J. Macheleid, *J. Phys. Chem.* 89 (1985) 2688. c) Salt-like triiodocyclopropenylidene iodide: R. Weiss, G.-E. Miess, A. Haller, W. Reinhardt, *Angew. Chem.* 98 (1986) 102; *Angew. Chem. Int. Ed. Engl.* 25 (1986) 103.
- [14] Compare the radical cation of CCl_4 : T. Drewello, T. Weiske, H. Schwarz, *Angew. Chem.* 97 (1985) 855; *Angew. Chem. Int. Ed. Engl.* 24 (1985) 869.

A Novel Electron Count and Metal-Metal Multiple Bonding in Trigonal Prismatic Clusters**

By Ralph A. Wheeler and Roald Hoffmann*

Kryuchkov, Kuzina and Spitsyn recently synthesized two trigonal prismatic clusters, $[\text{Tc}_6\text{Cl}_{12}]^{2\ominus}$ **1** and $[\text{Tc}_6\text{Cl}_{14}]^{3\ominus}$ **2**, whose structures were determined by Koz'min, Surazhskaya and Larina. Both clusters have novel electron counts and unusually short metal-metal bonds.^[1] **1** has 68 cluster electrons^[2] (32 metal electrons), with Tc-Tc distances of 2.21 Å along the prism axis and 2.57 Å along triangular faces. **2** has two weakly μ_3 -bound axial capping chloride ligands; if these are removed, $[\text{Tc}_6\text{Cl}_{12}]^{\ominus}$, with one electron less, is obtained. Relative to **1**, the short Tc-Tc distance in **2** is still shorter, and the longer one, in the triangles, still longer.



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These clusters stand at the intersection of two strong currents of modern inorganic chemistry—metal-metal multiple bonding and cluster electron counting rules. The short prism dimensions indicate metal-metal multiple bonding,^[3] and the cluster electron count is unique—compare, for example, octahedral $[\text{Mo}_6\text{Cl}_8]^{4\ominus}$ ($[\text{Mo}_6\text{Cl}_{14}]^{2\ominus}$, 24 cluster bonding electrons), $[\text{Ta}_6\text{Cl}_{12}]^{2\ominus}$ ($[\text{Ta}_6\text{Cl}_{18}]^{4\ominus}$, 16e), $[\text{Zr}_6\text{I}_{14}\text{C}]$ (14e), $[\text{Os}_6(\text{CO})_{18}]^{2\ominus}$ (14e); and trigonal prismatic $[\text{Rh}_6\text{C}(\text{CO})_{13}]^{2\ominus}$ (18e).^[4]

The Tc clusters thus have more electrons involved in metal-metal bonding than any other six-vertex clusters known. A detailed account of the bonding will be given elsewhere.^[5] Here we focus on the metal-metal bonding, which is conveniently described by noting in the cluster the three Tc_2 units, each with well-defined σ , π , δ , δ^* , π^* , and σ^* orbitals. Figure 1a shows the filled levels of **1**, labeled to indicate their bonding character within Tc_2 dimers.

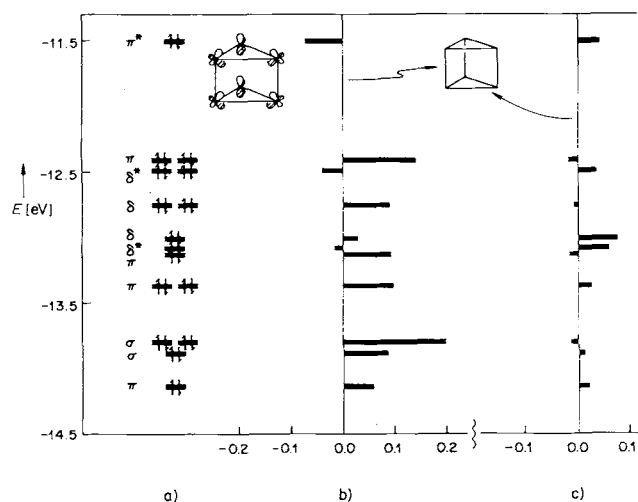


Fig. 1. a) Energy levels of the $[\text{Tc}_6\text{Cl}_{12}]^{2\ominus}$ cluster **1**. b) Orbital contributions to Tc-Tc overlap population within Tc-Tc dimers and (c) between them.

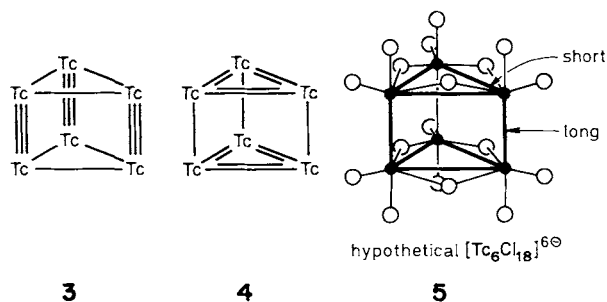
The lower 15 levels are three sets of σ , π_{xz} , π_{yz} , δ , and δ^* orbitals. The HOMO of **1** (schematically drawn at the top of Figure 1a) has π^* character within the Tc_2 units and π -bonding character between them. This description is consistent with electron-rich triple bonding ($\sigma^2\pi^4\delta^2\delta^{*2}$) within each Tc_2 unit, with two additional electrons in a π^* orbital. Bonding between Tc_2 units is primarily through the HOMO of the cluster (π bonding between dimers) and localized δ and δ^* orbitals (σ bonding between Tc_2 units).

The details of the bonding are neatly explored through examination of Figures 1b and 1c. The horizontal bars represent the contributions to the Tc-Tc overlap population of the corresponding levels in Figure 1a. Bonding within dimers (Fig. 1b) is much stronger than bonding between them (Fig. 1c). More levels are bonding in Figure 1b than in Figure 1c and their contributions to the overlap population are larger.

The observed bond-length changes on going from **1** to **2** (one-electron oxidation) are consistent with the composition of the HOMO. Figures 1b and 1c also show that the HOMO of $[\text{Tc}_6\text{Cl}_{12}]^{2\ominus}$ is net Tc-Tc antibonding, since its π^* nature within Tc_2 units wins out over its bonding character between them.

In reply to the question, how many metal-metal bonding electrons are there in this cluster?, we would answer 30. As the syntheses of **1** and **2** show (and the calculations sup-

port), 32 and 31 electrons, respectively, are also satisfactory. We expect that 30-electron compounds in this system will also be synthesized.



The 30 bonding electrons are in orbitals consistent with the localized description **3**. But since we know structures of the $[\text{Re}_3\text{Cl}_{12}]^{3\oplus}$ type,^[3] an alternative trigonal prismatic valence structure of type **4** is possible, which is realizable perhaps as $[\text{Tc}_6\text{Cl}_{18}]^{6\oplus}$ **5**.

The interconversion of **3** and **4** is strongly (symmetry) forbidden. Will we ever see isomeric structures such as these?

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CAS Registry numbers:
1, 101178-51-2; 2, 103752-27-8.

- [1] a) S. V. Kryuchov, A. F. Kuzina, V. I. Spitsyn, *Dokl. Akad. Nauk SSSR* 266 (1982) 127; b) for relevant crystallographic details, see P. A. Koz'min, M. D. Surazhskaya, T. B. Larina, *Koord. Khim.* 11 (1985) 1559. *Dokl. Akad. Nauk SSSR* 271 (1983) 1157.
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- [4] D. M. P. Mingos, *Chem. Soc. Rev.* 15 (1986) 31, and references cited therein; R. L. Johnston, D. M. P. Mingos, *Inorg. Chem.* 25 (1986) 1661.
- [5] R. A. Wheeler, R. Hoffmann, *J. Am. Chem. Soc.*, in press. Parameters for the extended Hückel calculations: Tc: $H_{ii}(5s) = -10.07$ eV, $H_{ii}(5p) = -5.40$, $H_{ii}(4d) = -12.82$ eV; Slater exponents $\zeta(5s) = 2.018$, $\zeta(5p) = 1.984$, $\zeta_1(4d) = 4.90$, $\zeta_2(4d) = 2.094$ with coefficients $C_1 = 0.5715$, $C_2 = 0.6012$. Cl: $H_{ii}(3s) = -30.0$, $H_{ii}(3p) = -15.0$ eV; Slater exponents $\zeta(3s) = \zeta(3p) = 2.033$. Geometrical parameters were taken from the crystal structure of **1** [1].

$[\text{La}\{(\text{Ph}_2\text{P})_2\text{CH}\}_3]$ — a Homoleptic Lanthanum Complex with π -Allyl-like Coordinated Diphosphinomethanide Ligands**

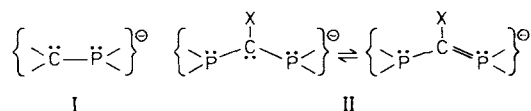
By Hans H. Karsch,* Armin Appelt, and Gerhard Müller*

Investigations of the chemistry of carbon and of σ -bonded phosphorus have revealed an increasing number of parallels in unsaturated systems.^[1] Also, for saturated systems, such parallels have been shown to be a valuable guide for structural comparison of molecules containing C-C and P-P bonds.^[2] The reactivities of the two elements in molecules containing P-C bonds are expected to be similar when the two elements are isoelectronic, as, for exam-

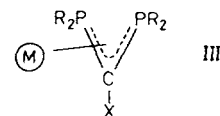
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[**] Complexes with Phosphinomethane and Phosphinomethanide Ligands,
Part 10. —Part 9: H. H. Karsch, B. Milewski-Mahrla, J. O. Besenhard, P.
K. Stauffert, P. Hofmann, T. A. Albright, *Inorg. Chem.*, in press.

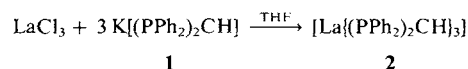
ple, in phosphinomethanides **I**. Indeed, in recent years a large number of ambident phosphinomethanides have been found in which carbon and phosphorus compete for electrophiles. Fine tuning of such systems may be effectively achieved by variation of the electrophile as well as of the number and kind of substituents on the carbanion.^[3,4]



With metals as electrophiles, coordination can occur in a variety of ways, including intermolecular interactions with formation of multinuclear complexes.^[3,4] For di- and triphosphinomethanides **II** (X = H, SiMe₃, PMe₂), in particular, numerous coordination modes may be envisaged.^[3,4] Already in the initial investigations,^[5] the main question was whether diphosphinomethanides **II** (X = H) form π -type complexes **III** with fragments M and thereby function as heteroallyl analogues. However, this type of coordination has not yet been unambiguously established. In comparing **II** with allyl ligands, it is important to realize that **II** (X = H) is a potential six-electron rather than a four-electron donor. A coordination of type **III** is opposed by the usually strong tendency of diphosphinomethanides to form M-P σ bonds in mononuclear complexes by coordinating both phosphorus atoms. Since lanthanoids and actinoids rarely form phosphane complexes,^[6] a coordination of type **III** should be favored with these metals.



Indeed, by reaction of the potassium salt **1**^[7] with LaCl_3 , we have been able to prepare the lanthanum complex **2**^[8] and to isolate it in pure form. Complex **2** is the first complex with π allyl-like η^3 -coordinated diphosphinomethanide ligands.



The X-ray structure analysis of **2**·toluene^[9] (Fig. 1) reveals that the La atom is trigonally planar coordinated by the diphosphinomethanide ligands. The midpoints of the PCP planes and the La atom lie in a plane (sum of angles at La: 360°, Fig. 1b). The distances between the central La atom and the coordinating atoms vary between 2.790(4) and 3.035(1) Å, the bonds to the C atoms being slightly shorter than those to the P atoms.^[10] As a consequence of these nearly identical distances, the lines connecting the midpoints of the ligands with the La atom are not exactly perpendicular to the respective PCP planes, but form angles with their normals of 16.9, 6.5, and 17.0°. Of the possible conformations, which differ in the relative orientation of the ligands, **2**·toluene has that in which the ligands are arranged spokelike around the central atom.

The orientations of the phenyl substituents indicate that the lone pairs of electrons on the phosphorus atoms do not point optimally in the direction of the La atom. As is evident from Figure 1b, however, further rotation about the HC-P bonds, which would be required for a better posi-