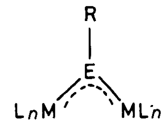
Three-membered Rings featuring Metal–Phosphorus Multiple Bonding

Atta M. Arif, Alan H. Cowley,* and Marek Pakulski

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

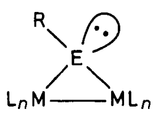
The reaction of $ArPCl_2$ (Ar = 2,4,6-$Bu^t{}_3C_6H_2$) with K[$Co(CO)_4$] or K[Mo(η-C_5H_5)$(CO)_3$] affords novel three-membered ring systems with metal–phosphorus bonding.

It has been established that two sixteen-electron organometallic fragments can bond to phosphinidenes or heavier congeners in an open (1)[1] or a closed (2)[2] fashion. From the standpoint of the main-group moiety, ER, the distinguishing feature of these structures is the involvement or non-involvement of the E lone pair electrons in the E–M bonding interaction. It occurred to us that, in the realm of fifteen-electron organometallic fragments, a similar bonding dichotomy should occur as represented by (3) and (4). We report examples of structure type (3)



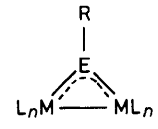
(1)

R = alkyl, aryl, halogen;
E = P, As, Sb, Bi;
ML_n = $Mn(CO)_2(\eta-C_5H_5)$, $M(CO)_5$
(M = Cr, Mo, W)

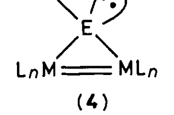


(2)

R = $(Me_3Si)_2CH$;
E = Sb;
L_nM = $Fe(CO)_4$



(3)



(4)

In a typical preparation, a solution of $K[Co(CO)_4]$ (12.0 mmol) in 130 ml of tetrahydrofuran (THF) was added dropwise to a solution of 6.0 mmol of $ArPCl_2$ (Ar = 2,4,6-$Bu^t{}_3C_6H_2$)[3] in 30 ml of THF at −40 °C. Separation of the crude product by column chromatography (silica gel/n-hexane) afforded the diphosphene ArP=PAr[3] and green, crystalline $ArP[Co(CO)_3]_2$ (**5**).† The 36.43 MHz $^{31}P\{^1H\}$ n.m.r. spectrum of (**5**) exhibited a broad (^{59}Co coupled) multiplet at δ + 664 p.p.m. An *X*-ray crystallographic study‡ revealed that each molecule of (**5**) resides on a site of C_{2v} symmetry, the aryl and PCo_2 planes being mutually perpendicular (Figure 1). The geometry at phosphorus is trigonal planar and the short P–Co bond length [2.047(6) Å] implies multiple bonding between these atoms. The Co–Co separation, on the other hand, [2.690(4) Å] is indicative of a single bond. The electronic structure of (**5**) can therefore be discussed in terms of (**6**) or canonical forms, (**7a,b**).

A similar compound, (**8**), can be prepared by the reaction of (2,4,6-$Bu^t{}_3C_6H_2$)PCl_2 with $K[(\eta-C_5H_5)Mo(CO)_3]$. The formulation for (**8**) is supported by the low-field ^{31}P n.m.r. chemical shift (s, δ +686 p.p.m.) and by preliminary *X*-ray work.

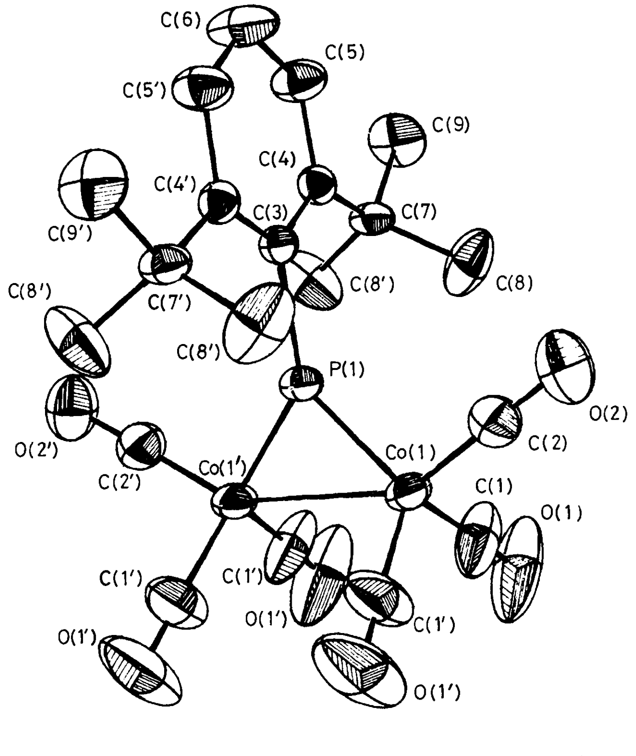
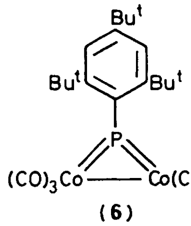
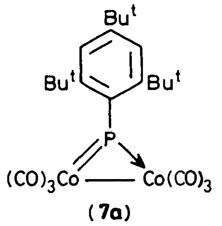


Figure 1. ORTEP view of (**5**) showing the atom numbering scheme. The *para*-Bu^t group is omitted because of disorder. Important parameters: Co(1)–Co(1') 2.690(4), Co(1)–P(1) 2.047(6) Å, Co(1)–P(1)–Co(1') 82.0(2), P(1)–Co(1)–Co(1') 49.1(2)°.

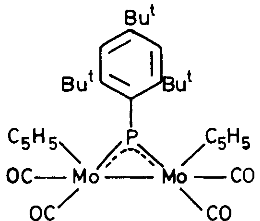


(**6**)

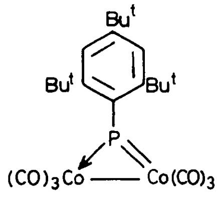


(**7a**)

↕



(**8**)



(**7b**)

From the point of view of fragment analysis, (**5**) and (**8**) can be regarded as the products of addition of a phosphinidene unit to a Co≡Co or Mo≡Mo bond. Recognising the isolobal relationship between C≡C and metal–metal triple bonds,[4] an interesting parallel can be seen between (**5**) and (**8**) and phosphirenes. Note, however, that phosphirenes adopt structure (**4**).[5]

Finally, we note with less bulky substituents, phosphinidenes form larger clusters such as $Co_3(\mu_3-PPh)(CO)_9$[6] and $Co_4(\mu_4-PPh)_2(\mu_2-CO)_2(CO)_8$.[7] In the cases of (**5**) and (**8**), the approach of additional organometallic moieties is inhibited by

---

† All new compounds had satisfactory chemical analyses and spectroscopic characteristics.

‡ *Crystal data* for (**5**): $C_{24}H_{29}Co_2PO_6$, a = 13.768(3), b = 18.736(2), c = 10.933(3) Å, U = 2820.2(5) Å^3, orthorhombic, space group *Cmcm* (No. 63), Z = 4, D_c = 1.324 g cm^{-3}, μ(Mo-K_α) = 12.6 cm^{-1}. Data were collected on an Enraf-Nonius CAD 4-F diffractometer over the range $2.0 \leqslant 2\theta \leqslant 50.0°$ at 293 K. Corrections for Lorentz and polarisation effects were applied but not for absorption or decay (<1.0%). From a total of 1416 unique reflections, 1372 [$I > 3.0\sigma(I)$] were considered observed and used to solve (direct methods) and refine (difference Fourier, full-matrix, least-squares) the structure of (**5**). The final least-squares refinement converged smoothly to give residuals R = 0.0907 and R_w = 0.1088. Note that the *para*-Bu^t group is disordered because of the C_{2v} site symmetry.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

the *ortho*-Bu^t groups. Structures akin to (**5**) and (**8**) may therefore be involved in the cluster building process.

We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support.

Received, 8th July 1985; Com. 972

References

1 For phosphinidene complexes, see G. Huttner, H.-D. Muller, A. Frank, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 705; K. M. Flynn, B. D. Murray, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 7460; H. Lang, L. Zsolnai, and G. Huttner, *Angew. Chem., Int. Ed Engl.*, 1983, **22**, 976; G. Huttner, J. Borm, and L. Zsolnai, *J. Organomet. Chem.*, 1984, **263**, C33; H. Lang, G. Mohr, O. Scheidsteger, and G. Huttner, *Chem. Ber.*, 1985, **118**, 574.

2 A. H. Cowley, N. C. Norman, and M. Pakulski, *J. Am. Chem. Soc.,* 1984, **106**, 6844.

3 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587; 1982, **104**, 6167.

4 M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148; R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711; F. G. A. Stone, *ibid.*, 1984, **23**, 89.

5 A. Marinetti and F. Mathey, *J. Am. Chem. Soc.*, 1982, **104**, 4484.

6 L. Markó and B. Markó, *Inorg. Chim. Acta*, 1975, **14**, L39; H. Beurich, T. Madach, F. Richter, and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 690.

7 R. C. Ryan and L. F. Dahl, *J. Am. Chem. Soc.*, 1975, **97**, 6904; R. C. Ryan, C. U. Pittman, and J. P. O'Connor, *J. Organomet. Chem.*, 1980, **193**, 247.