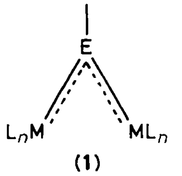
The Question of 'Open' or 'Closed' Bimetallic Phosphinidene (and Heavier Congeneric) Complexes

Atta M. Arif,[a] **Alan H. Cowley,**[a] **Nicholas C. Norman,**[b] **A. Guy Orpen,**[c] **and Marek Pakulski**[a]

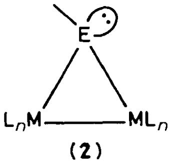
[a] *Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.*
[b] *Department of Chemistry, The University of Manchester, Manchester M13 9PL, U.K.*
[c] *Department of Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.*

The reaction of $ArPCl_2$ (Ar = 2,4,6-$Bu^t_3C_6H_2$) with $Na[Co_2(\mu_2\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ affords the 'open' phosphinidene complex, $Co_2(\mu_2\text{-}PAr)(\eta\text{-}C_5H_5)_2(CO)_2$, the structure of which has been determined by *X*-ray crystallography.

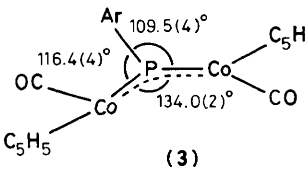
Bimetallic phosphinidene and heavier congeneric complexes can be written with 'open' (**1**) or 'closed' (**2**) structures. The former is distinguished by the absence of a M–M bond and a planar geometry around E whilst in the latter M–M bonding is present and the E atom is pyramidal. The several examples of 'open' structures feature the sixteen-electron organometallic fragments $Mn(CO)_2(\eta\text{-}C_5H_5)$ and $M(CO)_5$ (M = Cr, Mo, W).[1] So far, the only example of a 'closed' structure is $[Fe_2\{\mu\text{-}SbCH(SiMe_3)_2\}(CO)_8]$.[2] Reasoning that the preference for structure (**1**) or (**2**) might depend on the co-ordination number of M and/or the position of M in the transition series, we sought to prepare other 'closed' phosphinidene complexes by employing potentially hexaco-ordinate fragments involving later transition elements.



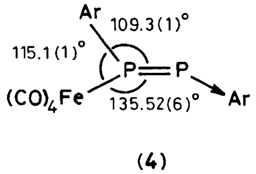
(1)



(2)



(3)



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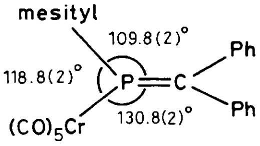

(5)

In a typical experiment, 4.0 mmol of $ArPCl_2$ (Ar = 2,4,6-$Bu^t_3C_6H_2$)[3] in 40 ml of tetrahydrofuran (THF) was added dropwise to 8.0 mmol of $Na[Co_2(\mu_2\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$[4] in 200 ml of THF at −40 °C. Separation of the crude reaction mixture by column chromatography (silica gel/n-hexane) afforded a 9% yield of ArP=PAr[3] and a 39% yield of dark blue crystalline $ArP[Co(CO)(\eta\text{-}C_5H_5)]_2$, (**3**). Somewhat surprisingly, an *X*-ray crystallographic study† established that (**3**) adopts an 'open' structure. Within experimental error, the geometry at phosphorus is trigonal planar and the Co---Co separation (3.89 Å) indicates that these atoms are not bonded. Moreover, the average P–Co bond length [2.110(4) Å] is suggestive of multiple bonding.[6] The difference in the P–Co bond lengths for (**3**) is virtually insignificant although there are appreciable distortions of the angles at phosphorus which resemble those for σ-diphosphene (**4**)[7] and σ-phospha-alkene (**5**)[8] complexes.

The ER 'inidine' fragment is strictly *isolobal* with CH^- but in the 'closed' form, *i.e.* (**2**), one electron pair is chemically innocent, leading to an analogy between the ER and CH_2 moieties. The 'closed' form, (**2**) is thus analogous to cyclopropane whilst the 'open' form, (**1**), is akin to the allyl anion.[9] The ER fragment may therefore be termed *ambilobal*, being isolobal with either CH^- or CH_2 in (**1**) and (**2**) respectively.

Preliminary Extended Hückel Molecular Orbital calculations on the model compound $[Fe_2(CO)_8(\mu\text{-}PH)]$ show that the isolobal analogy between the 'closed' form and the allyl anion is a faithful and accurate one and, moreover, that the 'open' form is slightly favoured in energy.

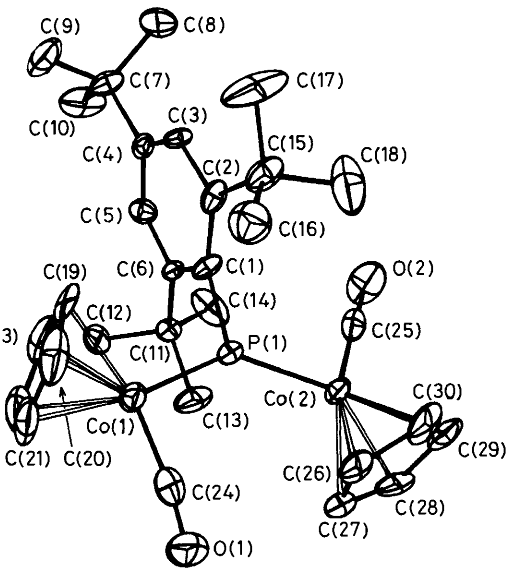

Figure 1. ORTEP view of (**3**) showing the atom numbering scheme. Important bond lengths include P–Co(1) 2.115(4), P–Co(2) 2.105(3), P–C(1) 1.852(13). See formula for bond angles.

The electronic conformational preference of the $d^8\text{-}ML_4$ fragment $\{Fe(CO)_4$ in $[Fe_2(CO)_8(\mu\text{-}PH)]$ and $Co(CO)(\eta\text{-}C_5H_5)$ in (**3**)} is shown to place the axial CO ligand(s) in the M_2ER plane for the 'open' geometry as observed for (**3**). Model building indicates, however, that this conformation is sterically difficult for R = $CH(SiMe_3)_2$ and E = Sb[2] but tenable for R = 2,4,6-$Bu^t_3C_6H_2$.

This combination of electronic and steric factors seems likely to determine the preferred geometry of these ambilobal species. Further synthetic and theoretical studies are in progress.

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† *Crystal data* for (**3**): $C_{30}H_{39}Co_2PO_2$, *a* = 10.184(3), *b* = 17.643(6), *c* = 8.790(5) Å, α = 92.21(4), β = 114.89(3), γ = 89.13(3)°, *U* = 1432 $Å^3$, triclinic, space group $P\bar{1}$ (No. 2), *Z* = 2, D_c = 1.35 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 12.3 cm^{-1}. Data were collected on an Enraf-Nonius CAD4-F diffractometer over the range $3.0 \leq 2\theta \leq 46.0°$ at 293K. Corrections for Lorentz, polarisation, and absorption effects were applied. From a total of 4278 unique measured reflections, 3972 [$I > 3.0\sigma(I)$] were considered observed and used to solve (Multan)[5] and refine (difference Fourier, full-matrix least-squares) the structure of (**3**). All non-hydrogen atoms were refined anisotropically. Final least squares refinement converged smoothly to give residuals *R* = 0.0641 and R_w = 0.0759.

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 IEW. Any request should be accompanied by the full literature citation for this communication.

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