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

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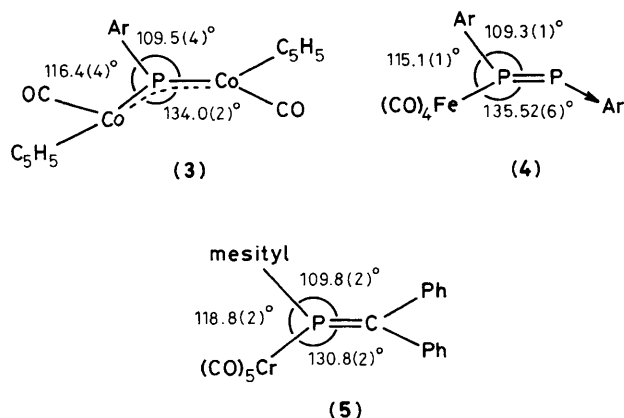[b] *Department of Chemistry, The University of Manchester, Manchester M13 9PL, U.K.*
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The reaction of $ArPCl_2$ (Ar = 2,4,6-$Bu^t_3C_6H_2$) with $Na[Co_2(\mu_2\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ affords the 'open' phosphinidene complex, $Co_2(\mu_2\text{-}PAr)(\eta\text{-}C_5H_5)_2(CO)_2$, 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

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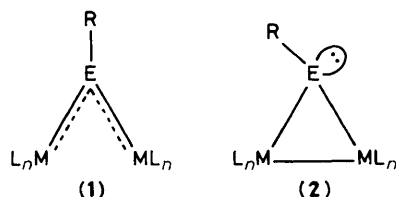
planar geometry around E whilst in the latter M–M bonding is present and the E atom is pyramidal. The several examples of 'open' structures feature the sixteen-electron organometallic fragments $Mn(CO)_2(\eta\text{-}C_5H_5)$ and $M(CO)_5$ (M = Cr, Mo, W).[1] So far, the only example of a 'closed' structure 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.
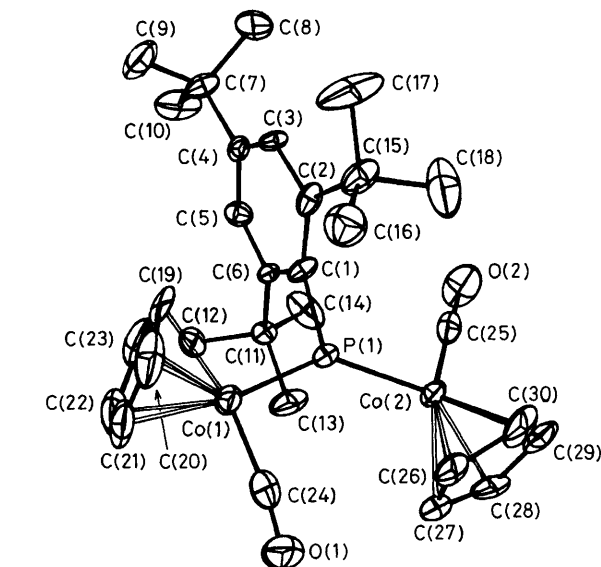
(3) (4)

(5)

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.

In a typical experiment, 4.0 mmol of ArPCl$_2$ (Ar = 2,4,6-Bu$^t_3$C$_6$H$_2$)[3] in 40 ml of tetrahydrofuran (THF) was added dropwise to 8.0 mmol of Na[Co$_2$(μ_2-CO)$_2$(η-C$_5$H$_5$)$_2$][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)(η-C$_5$H$_5$)]$_2$, (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)$_8$(μ-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.

The electronic conformational preference of the d^8-ML$_4$ fragment {Fe(CO)$_4$ in [Fe$_2$(CO)$_8$(μ-PH)] and Co(CO)(η-

C$_5$H$_5$) in (3)} is shown to place the axial CO ligand(s) in the M$_2$ER 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$^t_3$C$_6$H$_2$.

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.

References

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