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Preliminary Communication

Tetrahedrane cluster and phosphorus ligand activation in the reaction between $\text{PhCCo}_3(\text{CO})_9$ and 2,3-bis(diphenylphosphino)maleic anhydride. Molecular structure of $\text{Co}_3(\text{CO})_6(\mu_2-\eta^2-\eta^1-\text{C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O}))(\mu_2-\text{PPh}_2)$ (**2**).

$\text{Co}_3(\text{CO})_6(\mu_2-\eta^2-\eta^1-\text{C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O}))(\mu_2-\text{PPh}_2)$

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Abstract

The reaction of the μ_3 -benzylidyne capped cluster $\text{PhCCo}_3(\text{CO})_9$ (**1**) with 2,3-bis(diphenylphosphino)maleic anhydride (L-L) has been examined at 75 °C in toluene solvent. The major product isolated was not the expected diphosphine complex $\text{PhCCo}_3(\text{CO})_7(\text{L-L})$ but rather the new cluster $\text{Co}_3(\text{CO})_6(\mu_2-\eta^2-\eta^1-\text{C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O}))(\mu_2-\text{PPh}_2)$ (**2**). It is shown that the μ_3 -benzylidyne ligand in **1** is transformed into a bridging benzylidene ligand as a result of the formal insertion into one of the P-C bonds of the ancillary 2,3-bis(diphenylphosphino)maleic anhydride ligand. Formation of a μ_2 -phosphido group accompanies this transformation. Cluster **2** has been characterized by IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Single-crystal X-ray diffraction analysis establishes the presence of the new six-electron μ_2 -benzylidene- $\eta^2-\eta^1$ -(diphenylphosphino)maleic anhydride ligand. **2** crystallizes in the monoclinic space group $P2_1/n$, $a = 11.538(1)$, $b = 17.0754(8)$, $c = 19.506(1)$ Å, $\beta = 92.108(7)^\circ$, $Z = 4$, $D_{\text{calc}} = 1.557 \text{ g cm}^{-3}$, $R = 0.0392$, $R_w = 0.0432$ for 2012 observed reflections. Cluster **2** provides the experimental basis for enhanced μ_3 -C-Co bond reactivity as opposed to Co-Co bond reactivity. The significance of **2** is discussed in the context of cluster catalysis and ligand-modulated reactivity of the μ_3 -benzylidyne ligand in **1**.

The reactivity patterns of metal clusters in ligand substitution reactions are diverse [1]. The most com-

monly observed process is that of CO replacement by the incoming ligand. While the vast majority of ligand-substituted clusters are stable, there exist examples of facile activation sequences of the coordinated ligand that accompany the substitution reaction [2]. Knowledge of such ligand activation pathways is crucial to our greater understanding of the areas of metal cluster reactivity and cluster catalysis. During examination of the ligand substitution chemistry of $\text{PhCCo}_3(\text{CO})_9$ (**1**) [3] with 2,3-bis(diphenylphosphino)maleic anhydride (P-P) [4] we isolated the unexpected cluster $\text{Co}_3(\text{CO})_6(\mu_2-\eta^2-\eta^1-\text{C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O}))(\mu_2-\text{PPh}_2)$ (**2**). The novelty of this cluster resides in the facile activation of the μ_3 -benzylidyne capping ligand and its conversion to a μ_2 -benzylidene ligand in **2**. Such μ_3 -benzylidyne ligand behavior is unprecedented in this genre of cluster and is important as **2** may be invoked as a model for acylbenzylidene intermediates that have been postulated in the decarbonylation of acyl tricobalt clusters $\text{RC}(\text{O})\text{CCo}_3(\text{CO})_9$ and the decomposition of **1** and related clusters.

Treatment of **1** with 2,3-bis(diphenylphosphino)-maleic anhydride at 75 °C gives cluster **2** as the major product after chromatography**. **2** has been characterized in solution by IR and ^{31}P NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** exhibits two inequivalent ^{31}P resonances at δ 201.2 and 12.3, which are incompatible with either a chelating or bridging diphosphine ligand. The latter resonance is typical of a coordinated Co-PR₃ group while the former resonance suggests the presence of a μ_2 -phosphido moiety [5]. Accordingly, the structure of **2** was unequivocally determined by X-ray diffraction analysis[†]. Figure 1 shows the ORTEP diagram of cluster **2**. The six-electron μ_2 -

The thermolysis of 0.5 g (0.96 mmol) of $\text{PhCCo}_3(\text{CO})_9$ with 0.47 g (1.0 mmol) of 2,3-bis(diphenylphosphino)maleic anhydride was carried out in toluene at 75 °C. After 12 h, TLC analysis showed only a trace of cluster **1 and the presence of cluster **2** as the major product. **2** was isolated by chromatography on silica gel using CH_2Cl_2 . The analytical sample was recrystallized from benzene/isoctane (1:1) to afford 0.50 g (58% yield) of black **2**. IR (CH_2Cl_2) $\nu(\text{CO})$: 2062(m), 2042(vs), 2025(vs), 2010(sh), 1939(b, m), 1811(m), 1749(m) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 228 K) δ : 201.2 (μ_2 -phosphido) and 12.3 (phosphine). Anal. Calc. for $\text{C}_{41}\text{H}_{25}\text{Co}_3\text{O}_9\text{P}_2$: C, 54.69; H, 2.80. Found: C, 54.55; H, 2.88%. Crystals suitable for X-ray diffraction analysis were grown from a CH_2Cl_2 solution containing **2** that had been layered with heptane.

[†]Crystal data for **2**: space group $P2_1/n$; $a = 11.538(1)$, $b = 17.0754(8)$, $c = 19.506(1)$ Å, $\beta = 92.108(7)^\circ$, $Z = 4$, $D_{\text{calc}} = 1.557 \text{ g cm}^{-3}$, $\mu = 14.14 \text{ cm}^{-1}$, 5169 reflections were collected ($\text{Mo K}\alpha$, $2 \leq 2\theta \leq 44^\circ$) of which 2012 were observed, $R(F) = 0.0392$, $R_w(F) = 0.0432$. Diffraction measurements at 25 °C were made on an Enraf-Nonius CAD-4F diffractometer. The structure was solved by MULTAN and an absorption correction (DIFABS) was applied to the data. With the exception of the phosphorus phenyl carbons, all non-hydrogens were refined anisotropically. The hydrogen atoms were included in calculated positions with $B(\text{H}) = 1.3 B_{\text{eq}}(\text{C})$.

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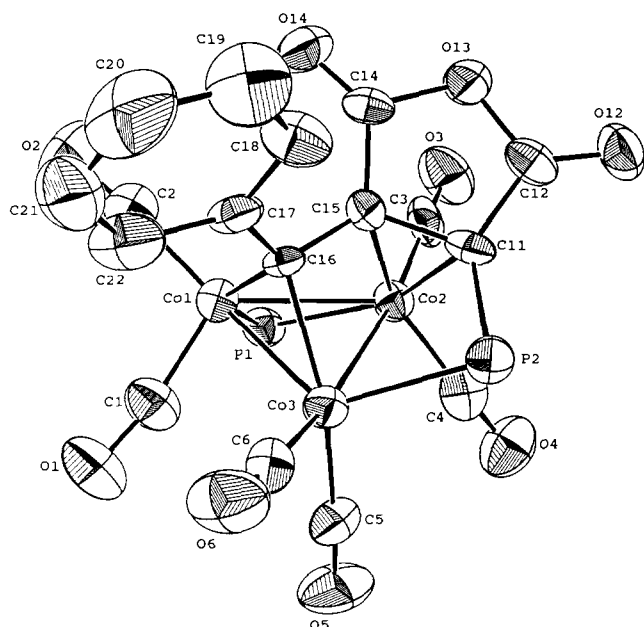


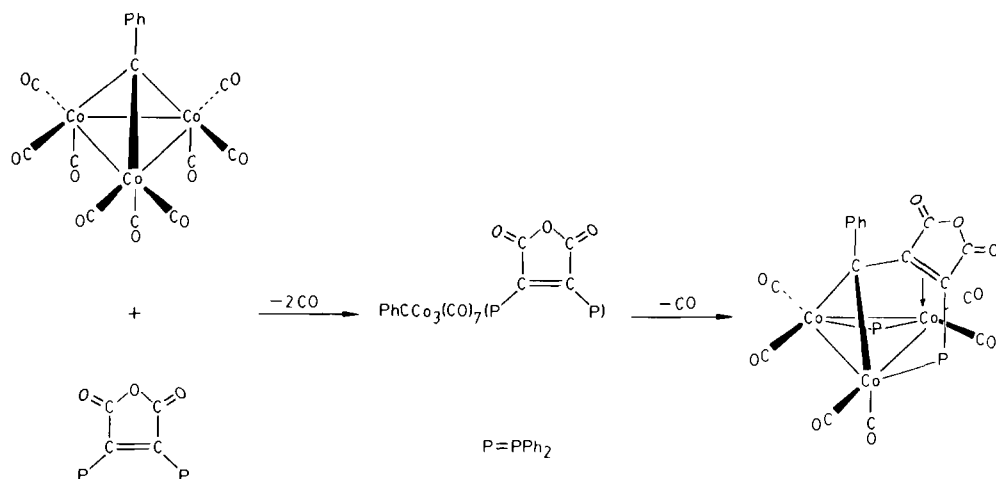
Fig. 1. ORTEP diagram of $\text{Co}_3(\text{CO})_6(\mu_2\text{-}\eta^2\text{-}\eta^1\text{-C(Ph)C=C(PPh}_2\text{)C(O)OC(O)})(\mu_2\text{-PPh}_2)$ (**2**). Selected bond distances (Å) and angles ($^\circ$) are $\text{Co}(1)\text{-Co}(2) = 2.576(2)$, $\text{Co}(2)\text{-Co}(3) = 2.696(2)$, $\text{Co}(1)\text{-Co}(3) = 2.412(2)$, $\text{Co}(1)\text{-P}(1) = 2.129(3)$, $\text{Co}(2)\text{-P}(1) = 2.264(3)$, $\text{Co}(1)\text{-C}(16) = 1.92(1)$, $\text{Co}(3)\text{-C}(16) = 2.023(9)$, $\text{Co}(1)\text{-C}(16)\text{-Co}(3) = 75.4(3)$ and $\text{Co}(1)\text{-P}(1)\text{-Co}(2) = 71.7(1)$. The phenyl groups associated with the phosphorus atoms have been omitted for clarity.

benzylidene- $\eta^2\text{-}\eta^1\text{-}$ (diphenylphosphino)maleic anhydride and the $\mu_2\text{-phosphido}$ ligands are clearly visible, accounting for the inequivalent ^{31}P resonances. Each cobalt atom is coordinatively saturated in agreement with other trinuclear 48-electron clusters.

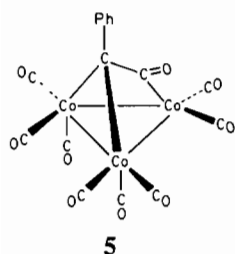
When the reaction between **1** and 2,3-bis(diphenylphosphino)maleic anhydride was monitored by IR spectroscopy no intermediates were observed. The putative $\text{PhCCo}_3(\text{CO})_7(\text{L-L})$ species, which is a

likely precursor to **2** [6], must undergo a rapid reaction to **2** as shown in Scheme 1. The coordinated 2,3-bis(diphenylphosphino)maleic anhydride ligand most likely facilitates the observed $\mu_3\text{-benzylidene/P-C}$ bond cleavage sequence [7] and evidence for this P-ligand activation comes from the independent isolation and characterization of the diphosphine-bridged cluster $\text{PhCCo}_3(\text{CO})_7(\text{cis-Ph}_2\text{PCH=CHPPh}_2)$ (**3**) [8], which is stable under analogous conditions. The only major difference expected between these diphosphine ligands would be electronic in origin. In keeping with **3**, the intermediate heptacarbonyl cluster $\text{PhCCo}_3(\text{CO})_7(\text{Ph}_2\text{P}\overline{\text{C}}=\text{C}(\text{PPh}_2)\text{C(O)OC(O)})$ must experience enhanced reactivity that derives from the unique electronic properties associated with the ancillary diphosphine ligand. Experiments designed to test this premise are planned and will be reported in due course.

The experimental identification of the $\mu_2\text{-benzylidene}$ moiety in **2** is of further importance as this allows cluster **2** to function as a model for a proposed intermediate in the fragmentation of **1** to $\text{Co}_2(\text{CO})_8$ (or $\text{HCo}(\text{CO})_4$) during hydroformylation catalysis [9]. While it is accepted that **1** and related clusters will fragment to lower nuclearity species under the appropriate conditions [10], the initial step in this multisequence fragmentation reaction is unknown. Clearly, a hapticity change associated with the capping $\mu_3\text{-benzylidene}$ ligand must be involved at some point in the reaction. Migratory insertion of a CO group into the $\mu_3\text{-benzylidene-Co}$ bond of **1** has been proposed during cluster attachment to $\text{SiO}_2\text{-Al}_2\text{O}_3$ [11, 12]. The resulting acylbenzylidene intermediate, which is shown below and is akin to **2**, was considered as a precursor to the C_6/C_7 hydrocarbons observed during cluster decomposition. Our successful isolation of cluster **2** lends support to the acylbenzylidene intermediate proposed by Meyers and Hall [11] and Gates *et al.* [13].



Scheme 1.



Future ligand substitution studies with other metal cluster complexes are planned in order to better assess the scope and reactivity of the 2,3-bis(diphenylphosphino)maleic anhydride ligand. It is anticipated that the new cluster systems will exhibit rich reactivity and redox chemistry.

Supplementary material

Tables of anisotropic thermal parameters (6 pages), bond lengths (3 pages), bond angles (5 pages) and structure factor amplitudes (23 pages) are available from the authors upon request.

Acknowledgements

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