Ligand-induced Scission of the Metal–Metal Bond in a Bicapped Tetracobalt Cluster

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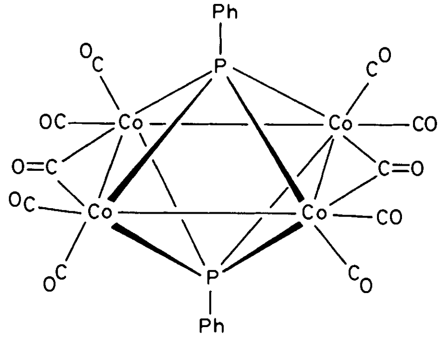
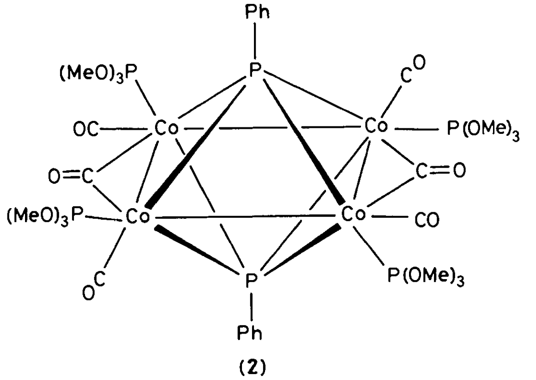
The catalytically active tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ undergoes Co–Co bond cleavage upon ligand substitution with the bidentate $F_2PN(Me)PF_2$.

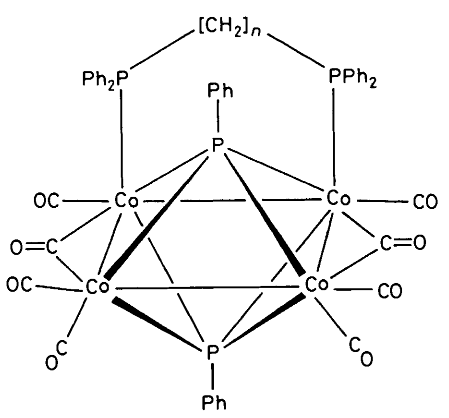
Polynuclear metal clusters continue to receive attention as potential catalysts, particularly for the utilization of CO.[1] The uniqueness of metal clusters in catalysis lies in the possibility of multisite activation of substrates induced by contiguous metal centres.[2—5] However the experimental basis for the cleavage of metal–metal bonds to provide such vacant metal sites on catalytically active clusters is generally lacking.[6]



(1)



(2)



(3)

n = 2 diphos
n = 1 dppm

We report a novel example of the ligand-induced cleavage of a metal–metal bond in the catalytically active tetranuclear cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$, (**1**).[7,8] This cluster benefits from the pair of capping μ_4-phosphinidene bridges which help to preserve the integrity of the tetracobalt array even upon the scission of a given metal–metal bond. Since strong nucleophiles are known to cleave polynuclear clusters (particularly of first-row transition metals) to species of lower nuclearity,[4,9] we examined the susceptibility of (**1**) towards various types of phosphine nucleophiles. Thus monofunctional phosphines such as trimethylphosphite $P(OMe)_3$ react stepwise to afford a series of four ligand substitution products $Co_4(CO)_{10-n}[P(OMe)_3]_n(\mu_4\text{-}PPh)_2$, in which the CO's on each cobalt centre have been successively replaced.[10] Structure (**2**) of the highest member ($n = 4$) is shown.

The bidentate ligands (diphos, $Ph_2PCH_2CH_2PPh_2$, and dppm, $Ph_2PCH_2PPh_2$) react in a single step to afford the cluster in which the ligand bridges the long metal–metal bond, typically shown as structure (**3**).[10] Attempts to force more extensive substitution led only to oligomeric products. On the other hand the bidentate fluorophosphine $F_2PN(Me)PF_2$ reacted smoothly with (**1**) to afford a single tetrasubstitution product, $Co_4(CO)_3[(F_2P)_2NMe]_4(\mu_4\text{-}PPh)_2$ (**4**), isolated in

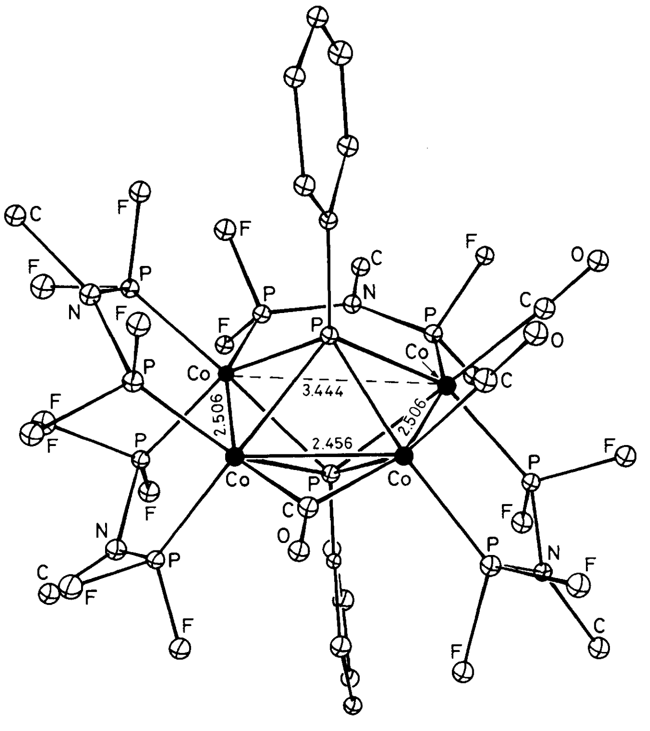


Figure 1. ORTEP diagram of the tetracobalt cluster $Co_4(CO)_3[(F_2P)_2NMe]_4(\mu_4\text{-}PPh)_2$ (**4**), showing the opening of the ring (3.44 Å, dashed lined). Hydrogens are omitted for clarity.

yields up to 70%.† The ORTEP diagram of (**4**) in Figure 1‡ shows that ligand substitution is accompanied by the scission of one Co–Co bond to a separation of 3.444 Å. Of the remaining Co–Co distances of 2.506 Å (those ligated by fluorophosphine) and 2.456 Å (that bridged by CO), the latter is the shortest known in this genre of clusters. [By comparison, the Co–Co distances in (**1**) are 2.520 and 2.698 Å for the CO bridged and unbridged bonds, respectively.[11]]

The unusual Co–Co bond cleavage in (**4**) probably results from the unique ligating ability and the strong π-acidity of the fluorophosphine ligand.[12] Indeed we hope that it will provide a mechanistic basis for developing a variety of activated metal clusters in which the catalytic sites are exposed without destroying the polynuclear integrity.

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† Typically, 0.7 mmol of (**1**) in 10 ml of benzene was treated with an excess of (5.5 mmol) of $F_2PN(Me)PF_2$ in a sealed Pyrex tube heated to *ca.* 55 °C overnight. T.l.c. examination (hexane : benzene, 8 : 2) of the product mixture revealed (**4**) as a slow-moving component (*ca.* 95% yield), which was isolated and recrystallized from n-hexane at −20 °C. Satisfactory elemental analysis was obtained. Note: only the tetrasubstituted cluster was observed even when 20 molar equivalents of the fluorophosphine ligand were employed at temperatures up to 85 °C. I.r. (CH_2Cl_2): 2021.3vs, 1988.1m, and 1817.2m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 3.10 (3H), 1.85 (9H), 6.96 (6H), 7.82 (4H). $^{31}P\{^1H\}$ N.m.r. ($CDCl_3$): δ 162.0 (bt, J_{P-F} 1160 Hz), −68.8 (bt, J_{P-F} 561 Hz).

‡ Space group *C*2/*c*; $a = 12.184(5)$, $b = 32.890(11)$, $c = 11.650(5)$ Å; $\beta = 111.60(3)°$; $Z = 4$; $R = 9.0\%$. There is a 50% disorder between one of the fluorophosphine ligands and the two carbonyls related by a two-fold axis, which remains even when refinement is done in space group *Cc*. This accounts for the poor scattering of the crystal and the somewhat high *R* value. 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.

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