shorter than the N–C single bond length of 1.472 Å.[11] It should be noted, however, that while the phenyl groups on one triazenide ligand [N(4)–N(6)] are almost coplanar with the N_3 plane, the phenyl groups on the other triazenide [N(1)–N(3)] are twisted (22° and 26°) with respect to the N_3 plane. The lack of significant variation in the N–C bond distances between the triazenide ligands, in spite of the difference in orientation of the phenyl rings, suggests that any delocalization of the N_3 π-system with the phenyl rings is relatively insensitive to torsion about the N–C bonds.

Compound 1 represents the first monomeric six-coordinate organometallic aluminum compound to be characterized structurally as well as the first observation of the trans influence in an aluminum compound.

Acknowledgment. Financial support of this work is provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and ICI, Wilton Materials Research Center, U.K. We thank Professor David Hoffman for useful discussion.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and bond distances and angles (5 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(11) (a) Sutton, L. E. *Interatomic Distances and Configuration in Molecules and Ions*; Special Publications No. 18; The Chemical Society: London, 1965. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Oxidative and Thermal Isomerization of Phosphido-Bridged Molybdenum Dicobalt Clusters: X-ray Crystal Structures of the Complexes $[MoCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ and $[NEt_4][MoCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$

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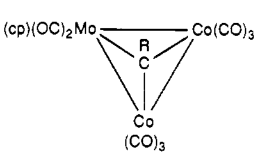
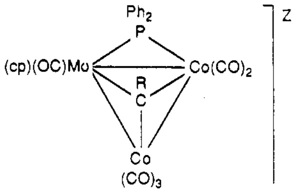
Summary: The anion 2^- undergoes two reversible one-electron oxidations, to 2 and 2^+, and is protonated to give 2-H which equilibrates with 3-H via thermal migration of the μ-PR_2 ligand; deprotonation of 2-H $\rightleftharpoons$ 3-H gives 3^- which is converted to 2 via a novel oxidatively induced μ-PR_2 migration reaction.

Treatment of metal carbonyl complexes with secondary phosphines can provide an efficient route for the synthesis of new phosphido-bridged derivatives.[1-3] The heterotrimetallic complexes $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[WCo_2(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) with PPh_2H give well-defined complexes $[WFe_2(\mu\text{-}H)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_7(\eta\text{-}C_5H_5)]$ and $[WCo_2(\mu\text{-}H)(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me), in which the μ-PPh_2 ligand bridges either the heteronuclear W–Fe or the homonuclear Co–Co bond, respectively.[4] Herein we report reactions on the $MoCo_2$ complex 1 which show that μ-PPh_2 ligands may undergo novel redox-induced dynamic behaviour leading to facile interconversion of isomers in which the μ-PPh_2 ligand bridges either the homonuclear Co–Co or the heteronuclear Mo–Co bond.

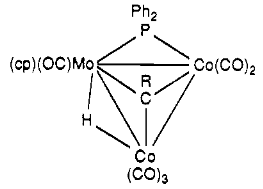
Treatment of 1 with 1 equiv of $LiPPh_2$ in tetrahydrofuran gives a highly reactive anion 2^- which is readily oxidised by air or $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ affording the stable 47 cluster valence electron radical 2.[5] The cyclic voltammogram[6] (CV) of 2 shows the expected reversible one-electron reduction to 2^- ($E°$ = −0.55 V) and also reveals a reversible one-electron oxidation to 2^+ ($E°$ = 0.39 V). The structure of the radical 2 was established by a single-crystal X-ray diffraction study[7] which confirms that the μ-PPh_2 ligand bridges a Mo–Co bond (Figure 1). The reversibility of the CV waves described above implies that no gross structural rearrangement takes place on oxidation or reduction.



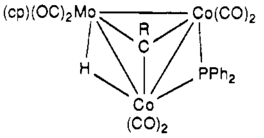
(1)



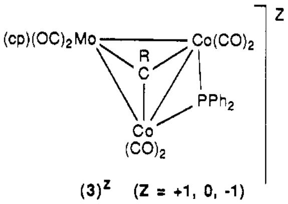
$(2)^z$ (Z = +1, 0, −1)



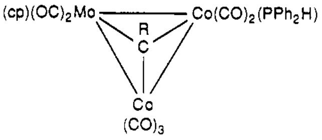
(2)-H



(3)-H



$(3)^z$ (Z = +1, 0, −1)



(4)

R = C_6H_4Me-4, cp = (η-C_5H_5)

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(1) Henrick, K.; Horton, A. D.; McPartlin, M.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1083 and references therein.

(2) Colbran, S. B.; Johnson, B. F. G.; Lewis, J.; Sorrel, R. M. *J. Organomet. Chem.* **1985**, *296*, C1.

(3) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *Organometallics* **1984**, *3*, 392.

(4) Jeffery, J. C.; Lawrence-Smith, J. G. *J. Chem. Soc., Chem. Commun.* **1985**, *275*; **1986**, 17. Dunn, P.; Jeffery, J. C.; Sherwood, P. *J. Organomet. Chem.* **1986**, *311*, C55. Jeffery, J. C.; Lawrence-Smith, J. G. *J. Organomet. Chem.* **1985**, *280*, C34.

(5) Selected spectroscopic data (^1H NMR in CD_2Cl_2, and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR in CD_2Cl_2–CH_2Cl_2 unless otherwise noted; coupling constants in Hz). Compound 2^-: IR (ν_{CO}(max), CH_2Cl_2) 2003 s, 1944 vs, 1893 m, 1849 w, sh cm^{-1}; $^{31}P\{^1H\}$ δ 170.9 (MoCo(μ-P)) ppm. Compound 2: IR (ν_{CO}(max), CH_2Cl_2) 2055 s, 2002 vs, br, 1887 w, br cm^{-1}. Compound 2^+: IR (ν_{CO}(max), CH_2Cl_2) 2094 s, 2054 vs, 2004 vs, 1920 cm^{-1}. Compound 2-H: IR (ν_{CO}(max), CH_2Cl_2) 2054 s, 2020 vs, 1984 s, sh, 1880 w, br cm^{-1}; ^1H NMR δ −13.56 [d, 1 H, μ-H, J(PH) = 12]; $^{31}P\{^1H\}$ δ 196.4 ppm (MoCo(μ-P)); $^{13}C\{^1H\}$ δ 255.2 [d, μ-CR, J(PC) = 22], 228.8 [d, MoCO, J(PC) = 17]. Compound 3-H: IR (ν_{CO}(max), CH_2Cl_2) 2039 m, 2010 vs, 1982 s, 1860 w, br cm^{-1}; ^1H NMR δ −13.34 [d, 1 H, μ-H, J(PH) = 22]; $^{31}P\{^1H\}$ δ 229.5 ppm (br, Co_2(μ-P)); $^{13}C\{^1H\}$ δ 256.9 [d, μ-CR, J(PC) = 24], 238.1, 220.5 (2 × s, 2 × MoCO). Compound 3^-: IR, (ν_{CO}(max), CH_2Cl_2) 1989 s, 1950 vs, 1924 s, 1840 br, 1800 w, br cm^{-1}; $^{31}P\{^1H\}$ δ 178.2 ppm (Co_2(μ-P)); $^{13}C\{^1H\}$ δ 264.5 [d, μ-CR, J(PC) = 17]. Compound 3: IR (ν_{CO}(max), CH_2Cl_2) 2032 m, 1988 vs, 1956 m, 1923 w, br, and 1870 w, br cm^{-1}. Compound 4: IR (ν_{CO}(max), CH_2Cl_2) 2049 m, 2010 s, 2002 s, 1989 s, 1912 w, br cm^{-1}; $^{31}P\{^1H\}$, δ 38.7 ppm (br, PPh_2H); $^{13}C\{^1H\}$ δ 262.0 (μ-CR).

(6) Cyclic voltammetry was carried out at a platinum bead electrode in CH_2Cl_2 0.1 mol dm^{-3} in $[NBu^n_4][PF_6]$ as supporting electrolyte. Potentials are quoted vs the saturated calomel electrode; $E°$ for the oxidation of ferrocene, added as an internal standard, was 0.47 V under the experimental conditions used.

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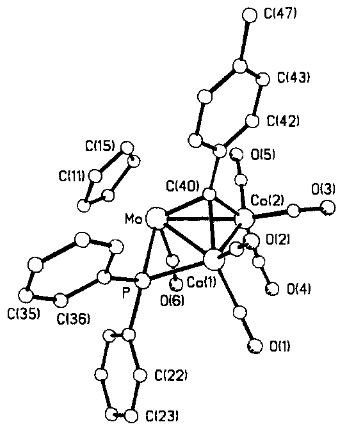

Figure 1. Molecular structure of [MoCo$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-PPh$_2$)(CO)$_6$(η-C$_5$H$_5$)] (**2**). Dimensions: Mo–Co(1) = 2.572 (3), Mo–Co(2) = 2.785 (3), Mo–P = 2.369 (5), Mo–C(40) = 1.99 (2), Co(1)–Co(2) = 2.478 (4), Co(1)–P = 2.231 (6), Co(1)–C(40) = 2.01 (2), Co(2)–C(40) = 1.92 (2) Å; Co(1)–Mo–Co(2) = 54.9 (1), Mo–Co(1)–Co(2) = 66.9 (1), Mo–Co(2)–Co(1) = 58.2 (1), Mo–P–Co(1) = 67.9 (2), Mo–C(40)–C(41) = 135 (1), Co(1)–C(40)–C(41) = 128 (1), Co(2)–C(40)–C(41) = 126 (1)°.

Low-temperature protonation of **2**$^-$ (HBF$_4$·Et$_2$O, 0 °C) gives the μ-hydrido derivative **2-H**. At ambient temperature, solutions of **2-H** slowly (ca. 2 h) equilibrate with a new isomer **3-H** (**2-H**:**3-H** = 1:4), a process requiring thermally induced migration of the μ-PPh$_2$ ligand between the Mo–Co and Co–Co bonds. Treatment of **1** with 1 equivalent of PPh$_2$H initially affords the terminal PPh$_2$H complex **4** which smoothly rearranges (Et$_2$O, 35 °C) to the same (1:4) mixture of **2-H** and **3-H** obtained from protonation of **2**$^-$.

Deprotonation of **2-H** and **3-H** (KOH–EtOH) gives a comparatively stable anion **3**$^-$ which was readily isolated as its tetraethylammonium salt. The structure of **3**$^-$ was established by a single-crystal X-ray diffraction study[7] which confirms that the μ-PPh$_2$ ligand bridges the homonuclear Co–Co bond (Figure 2). The CV of **3**$^-$ (Figure 3) shows two oxidation waves in the potential range –0.9 to 0.7 V. The first wave ($E°$ = –0.31 V) is fully reversible (Figure 3a) and corresponds simply to the formation of **3**. Multiple scanning (Figure 3b) through the second wave, however, shows that *rapid* isomerization occurs, via μ-PPh$_2$ bridge migration, after the formation of **3**$^+$, giving **2**$^+$; the reversible product wave centered at –0.55 V is identical with that for the couple **2**–**2**$^-$.[8]

The chemical oxidation of **3**$^-$ is also consistent with the processes shown in Scheme I. The weak oxidant [C$_7$H$_7$][BF$_4$] (tropylium tetrafluoroborate) ($E°$ = –0.18 V, in MeCN[9]) and **3**$^-$ in tetrahydrofuran gave **3** which, once isolated, only slowly rearranged to **2**. However, the addition of slightly more than 1 equiv of [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] ($E°$ = 0.47 V) to **3**$^-$ rapidly gave **2**. In this case, the conversion of **3** to **2** can be catalyzed via the formation of **3**$^+$.[10]

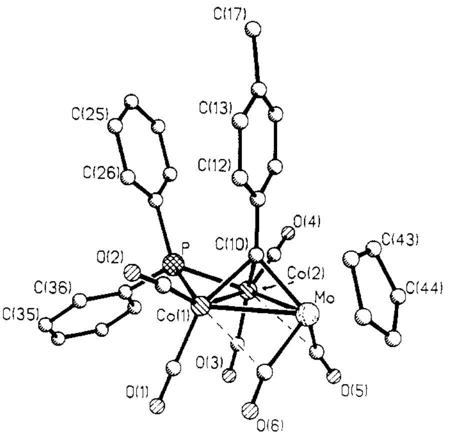

Figure 2. Molecular structure of [NEt$_4$][MoCo$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-PPh$_2$)(CO)$_6$(η-C$_5$H$_5$)] (**3**$^-$). Dimensions: Mo–Co(1) = 2.741 (2), Mo–Co(2) = 2.761 (2), Mo–C(10) = 2.05 (1), Co(1)–Co(2) = 2.415 (2), Co(1)–P = 2.176 (3), Co(1)–C(10) = 1.964 (9), Co(2)–P = 2.175 (3), Co(2)–C(10) = 1.965 (9) Å; Co(1)–Mo–Co(2) = 52.1 (1), Mo–Co(1)–Co(2) = 64.4 (1), Mo–Co(2)–Co(1) = 63.5 (1), Co(1)–P–Co(2) = 67.4 (1), Mo–C(10)–C(11) = 130.2 (6), Co(1)–C(10)–C(11) = 129.2 (7), Co(2)–C(10)–C(11) = 130.6 (7)°.

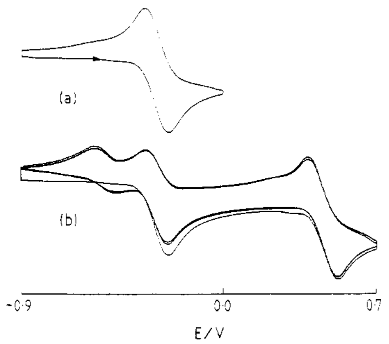

Figure 3. The cyclic voltammogram of **3**$^-$ in CH$_2$Cl$_2$ at a platinum bead electrode: (a) single scan from –0.9 to 0.0 V and (b) multiple scan from –0.9 to +0.7 V.

Scheme I

$$\begin{tikzcd}
(2)^- \arrow[r, shift left, "-e^-"] & (2) \arrow[l, shift left, "+e^-"] \arrow[r, shift left, "-e^-"] & (2)^+ \arrow[l, shift left, "+e^-"] \\
(3)^- \arrow[r, shift left, "-e^-"] & (3) \arrow[l, shift left, "+e^-"] \arrow[r, shift left, "-e^-"] \arrow[u, "slow"] & (3)^+ \arrow[l, shift left, "+e^-"] \arrow[u, "fast"]
\end{tikzcd}$$

These reactions demonstrate that it is possible to isolate both kinetically (**2**$^-$ and **3**) and thermodynamically (**2** and **3**$^-$) stable μ-PPh$_2$-bridged clusters. The mechanism of μ-PPh$_2$ bridge migration might involve a bridge–terminal–bridge process similar to that observed for carbonyl and nitrosyl ligands. In the case of the μ-H derivatives **2-H** and **3-H**, we cannot rule out the possibility that isomerisation proceeds via terminal PPh$_2$H intermediates generated by retromigration of the μ-H ligands to phosphorus. Some support for this suggestion is given by the observation that treatment of **2-H** and **3-H** with CO readily regenerates **4**.

Acknowledgment. We thank the SERC for support (to M.R.B.).

Supplementary Material Available: Crystal data and tables of interatomic distances and angles, positional parameters, and anisotropic thermal parameters (13 pages); listings of observed and calculated structure amplitudes (34 pages). Ordering information is given on any current masthead page.

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(7) Crystal data for **2**: C$_{31}$H$_{22}$Co$_2$MoO$_6$P, M = 735.3; orthorhombic, space group $Pbca$; a = 16.350 (6), b = 17.523 (6), c = 20.731 (11) Å; U = 5939 (4) Å^3; Z = 8; D_{calcd} = 1.64 g cm^{-3}; $F(000)$ = 2936; μ(Mo Kα) = 16.03 cm^{-1}. Current R = 0.076 (R_w = 0.071) for 1575 absorption-corrected intensities [293 K, Wyckoff ω-scans, $2\theta \leqslant 40°$, $F \geqslant 4\sigma(F)$, Nicolet P3 diffractometer, Mo Kα ($\bar{\lambda}$ = 0.71069 Å)]. Crystal data for **3**$^-$: C$_{39}$H$_{42}$Co$_2$MoNO$_6$P, M = 865.5; monoclinic, space group $P2_1/c$; a = 13.538 (4), b = 11.509 (3), c = 25.250 (9) Å; β = 104.36 (3)°; U = 3811 (2) Å^3; Z = 4; D_{calcd} = 1.51 g cm^{-3}; $F(000)$ = 1768; μ(Mo Kα) = 12.6 cm^{-1}. Current R = 0.072 (R_w = 0.068) for 3473 absorption-corrected intensities [293 K, Wyckoff ω-scans, $2\theta \leqslant 50°$, $F \geqslant 4\sigma(F)$, Nicolet P3 diffractometer].

(8) The second oxidation wave is a composite wave corresponding to the couples **3**$^+$–**3** ($E°$ = ca. 0.44 V) and **2**$^+$–**2** ($E°$ = 0.39 V); the reversibility of either individual wave is impossible to establish from the cyclic voltammogram.

(9) Wasielewski, M. R., Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222.

(10) Generation of small quantities of **3**$^+$ from **3** by the stronger oxidant (cf. the tropylium ion) is followed by fast isomerization to **2**$^+$. The cross reaction **2**$^+$ + **3** $\rightleftharpoons$ **2** + **3**$^+$ then regenerates **3**$^+$ and affords **2** as the final product.