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Preliminary communication

Ligand-centred coupling of the alkynyl radical cations $[Mo(C{\equiv}CR)(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_7H_7)]^+$ (R = Ph or Bu^n): crystal structure of the dimeric product $[Mo_2(Ph_2PCH_2CH_2PPh_2)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4R_2)][PF_6]_2$ (R = Ph)

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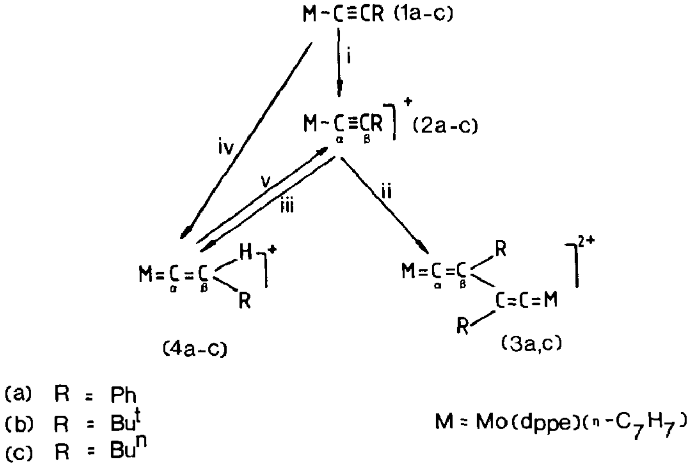
Abstract

The radical cations $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$ (R = Ph or Bu^n; dppe = $Ph_2PCH_2CH_2PPh_2$) undergo coupling at C_β of the alkynyl ligand to afford the divinylidene-bridged, dimeric products $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4R_2)]^{2+}$, characterised crystallographically for R = Ph.

The participation of radical cation intermediates in oxidatively-induced, ligand-centred dimerisation reactions of organometallic complexes has been suggested by



Scheme 1. Reagents and conditions: i, $[Fe(\eta\text{-}C_5H_5)_2]^+$ in CH_2Cl_2; ii, R = Ph or Bu^n; stir in thf or CH_2Cl_2; iii, R = Bu^t only, stir in thf; iv, HBF_4 in Et_2O; v, R = Ph, copper(II) acetate in methanol.

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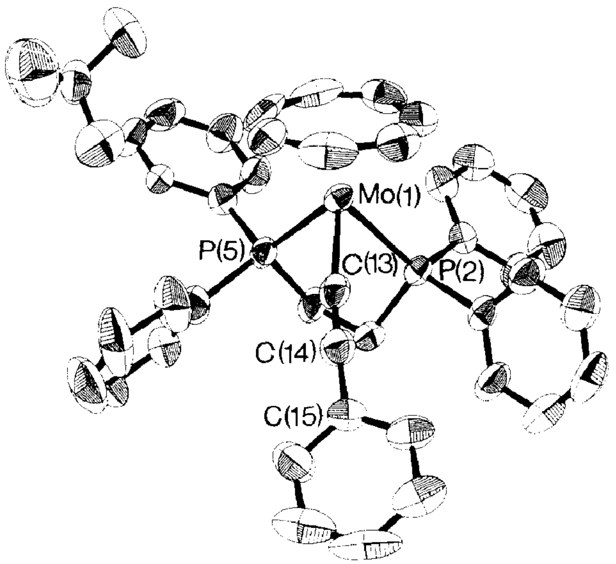

Fig. 1. ORTEP [7] plot of the molecular structure of **2a**-[BF$_4$]. Important dimensions include: bond lengths (Å) Mo(1)–C(13) 2.067(9), Mo(1)–P(2) 2.538(2), Mo(1)–P(5) 2.528(3), C(13)–C(14) 1.196(11), C(14)–C(15) 1.445(12); bond angles (°) Mo–(1)–C(13)–C(14) 174.6(8), C(13)–C(14)–C(15) 175.0(10).

several authors [1–3]. However in all previous examples these radicals have been extremely transient species, far too reactive for detailed characterisation. We now present new evidence to support the involvement of radical intermediates in dimerisation processes, namely the observation of the ligand-centred coupling of an isolated and fully characterised organometallic alkynyl radical cation.

We have previously described [4] the synthesis and isolation of the alkynyl radicals [Mo(C≡CR)(dppe)(η-C$_7$H$_7$)]$^+$ (**2a**: R = Ph; **2b**; R = Bu^t) (see Scheme 1) and now provide absolute confirmation of their identities through determination of a single crystal X-ray structure * for the tetrafluoroborate salt of **2a** (Fig. 1). The alkynyl bond length of **2a**, C(13)–C(14), is virtually identical to that found for the diamagnetic precursor complex **1a** [5], but one-electron oxidation does give rise to a decrease of 0.07(1) Å in the Mo(1)–C(13) bond length and a small bending away from linearity of Mo(1)–C(13)–C(14).

Prolonged stirring of **2a**-[BF$_4$] in CH$_2$Cl$_2$ results in a colour change from blue to deep red and the formation of low yields of diamagnetic [Mo$_2$(dppe)$_2$(η-C$_7$H$_7$)$_2$(μ-

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* Crystal data for **2a**-[BF$_4$]: C$_{41}$H$_{36}$MoP$_2$BF$_4$, M = 772.7, monoclinic, space group $P2_1/c$ (No. 14), a 10.412(2), b 15.104(1), c 22.981(2) Å, β 97.90(2)°, V 3579.8 Å^3, T 294 K, Z = 4, D_c 1.43 g cm^{-3}, F(000) = 1580, μ(Mo-K_α) 5.4 cm^{-1}. 5520 unique reflections, 2787 with $F > 3\sigma(F)$ used in refinement, final R = 0.0599. Crystal data for **3a**-[PF$_6$]$_2$: C$_{82}$H$_{72}$Mo$_2$P$_6$F$_{12}$, M = 1663.2, monoclinic, space group $P2_1/c$ (No. 14), a 16.399(4), b 12.365(4), c 20.577(6) Å, β 122.21(2)°, V 3530.3 Å^3, T 294 K, Z = 2, D_c 1.56 g cm^{-3}, F(000) = 1692, μ(Mo-K_α) 6.1 cm^{-1}. 6275 unique reflections, 3759 with $F > 3\sigma(F)$ used in refinement, final R = 0.0480.

Intensity data were collected on an Enraf–Nonius CAD 4 diffractometer using Mo-K_α X-radiation (λ 0.71069 Å). Structures were solved by heavy atom (Patterson and Fourier) methods and refined by least squares.

Tables of atomic coordinates, bond lengths and angles, and structure factors for **2a** and **3a** have been deposited with the Cambridge Crystallographic Data Centre.

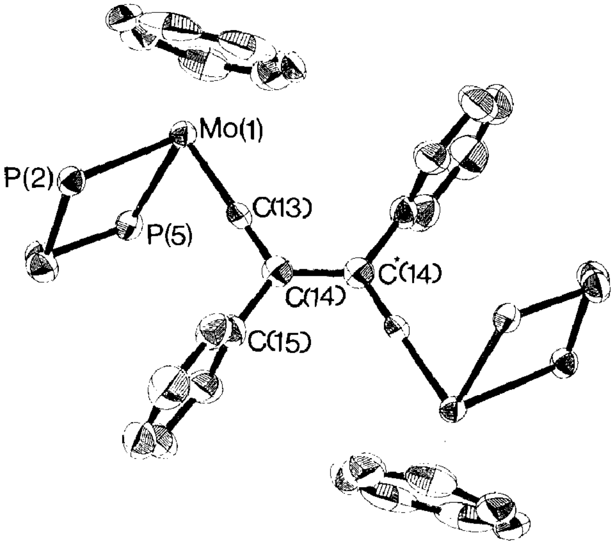

Fig. 2. ORTEP [7] plot of the molecular structure of **3a**-$[PF_6]_2$. Phenyl groups attached to P(2) and P(5) and the counter anions $[PF_6]$ are omitted for clarity. Important dimensions include: bond lengths (Å) Mo(1)–C(13) 1.951(5), Mo(1)–P(2) 2.528(1), Mo(1)–P(5) 2.550(2), C(13)–C(14) 1.353(7), C(14)–C*(14) 1.472(12), C(14)–C(15) 1.498(7); bond angles (°) Mo(1)–C(13)–C(14) 177.9(4), C(13)–C(14)–C*(14) 123.8(9), C(13)–C(14)–C(15) 116.7(5). C*(14)–C(14)–C(15) 119.3(5).

$C_4Ph_2)]^{2+}$ (**3a**), which is more effectively prepared when **2a**-$[PF_6]$ is stirred for 24 h in tetrahydrofuran (thf). Spectroscopic data * for **3a** did not permit a full structural assignment and therefore an X-ray crystallographic study was carried out. Analysis of the molecular structure of **3a** as a hexafluorophosphate salt (Fig. 2) reveals the formation of a new carbon–carbon bond C(14)–C*(14) via coupling of two molecules of **2a** at C_β of the alkynyl ligand to give a dimeric product in which a 2,3-diphenyl-1,3-butadien-1,4-diylidene ligand bridges the two molybdenum centres. In contrast to the related dimer [3] $[Fe_2(dppe)_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_4Me_2)][BF_4]_2$, in **3a** C(14)–C*(14) defines a molecular centre of symmetry and furthermore the dihedral

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* Satisfactory microanalytical data were obtained for all new complexes, NMR data recorded in CD_3CN, coupling constants in Hz. The identity of the hexafluorophosphate salts of **2a** and **2b** (previously characterised as $[BF_4]$ salts [4]) was also confirmed by IR and ESR spectroscopy.

Selected data. **1c**: brown solid, $\nu(C{\equiv}C)$ (CH_2Cl_2) 2068 cm^{-1}, $E^{\ominus}$ -0.25 V vs. SCE by cyclic voltammetry in CH_2Cl_2, experimental conditions as in ref. 4.

3a-$[PF_6]_2$: deep red solid, yield from **2a**-$[PF_6]$ 54% ^1H NMR δ 8.04–5.44, m, Ph, δ 4.37(t, J(P–H) 3 Hz, C_7H_7), δ 2.65, 1.77, br, CH_2. ^{13}C NMR δ 139.0–128.8, Ph and C_β, δ 93.4, C_7H_7, δ 28.3 (AA′X, ^1J(P–C)+^2J(P–C) = 35 Hz, CH_2) poor solubility precluded observation of C_α.

3c-$[PF_6]_2$: deep purple solid, yield from **1c** 43% ^1H NMR δ 7.91–7.36, m, Ph, δ 4.80, C_7H_7, δ 3.12, 2.84, br, CH_2(dppe), δ 0.84, 0.26, -0.10 Bu^n. ^{13}C NMR δ 375.9(t, J(P–C) 25 Hz, C_α), δ 137.2–126.4, Ph and C_β, δ 91.7, C_7H_7, δ 32.1, 29.9, 23.6, 13.6 Bu^n, δ 26.6 (AA′X, ^1J(P–C)+^2J(P–C) = 38 Hz, CH_2(dppe)). Spectroscopic data for **3c** were distinct from that for mononuclear $[Mo(C{=}CHBu^n)(dppe)(\eta\text{-}C_7H_7)]^+$ (**4c**) which was independently prepared and characterised as an orange solid.

4b-$[BF_4]$ orange solid, yield from **1b** 28%. ^1H NMR δ 7.96–7.35 m, Ph, δ 5.26(t, J(P–H) 3 Hz, C_7H_7), δ 4.37(t, J(P–H) 12 Hz, C*H*Bu^t), δ 2.58, br, CH_2(dppe), δ 0.55, s, Bu^t. ^{13}C NMR δ 368.0(t, J(P–C) 31 Hz, C_α), δ 136.6–127.4, Ph and C_β, δ 91.3, C_7H_7, δ 35.5(t, J(P–C) 6 Hz, *C*Me$_3$), δ 29.2 C*Me*$_3$, δ 25.0 (AA′X, ^1J(P–C)+^2J(P–C) = 41 Hz, CH_2(dppe)).

angle between planes comprising [CHO–Mo(1)–C(13)] * and [C(13)–C(14)–C★(14)–C(15)] is 19.1°; thus in the solid state the arrangement of the divinylidene bridge approximates to that of a highly unusual vertical conformation [6]. The reaction sequence **2a** → **3a** is especially pertinent to the work of Selegue et al. [3] in which the alkynyl radical $[Fe(C{\equiv}CMe)(dppe)(\eta\text{-}C_5H_5)]^+$ was proposed, but not substantiated, as an intermediate in the formation of $[Fe_2(dppe)_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_4Me_2)][BF_4]_2$ from reaction of $[Fe(C{=}CHMe)(dppe)(\eta\text{-}C_5H_5)][BF_4]$ with iodosobenzene or copper(II) acetate. Moreover, on account of the relative stability of the cycloheptatrienylmolybdenum radical **2a**, we can demonstrate its formation on treatment of the mononuclear vinylidene $[Mo(C{=}CHPh)(dppe)(\eta\text{-}C_7H_7)]^+$ (**4a**) [4] with copper(II) acetate.

The reactivity of the radicals **2** is critically dependent upon the alkynyl substituent. Thus one-electron oxidation of $[Mo(C{\equiv}CBu^n)(dppe)(\eta\text{-}C_7H_7)]$ (**1c**) with $[Fe(\eta\text{-}C_5H_5)_2][PF_5]$ in CH_2Cl_2 affords the transient radical (**2c**) (IR $\nu(C{\equiv}C)(CH_2Cl_2)$ 2055 cm^{-1}; ESR (CH_2Cl_2) $g_{av.} = 1.995$, $A(^{31}P)$ 23 gauss]. On attempted isolation **2c** yields a deep-purple diamagnetic product which, in view of the known structure of **3a**, was formulated as dimeric $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Bu^n{}_2)]^{2+}$ (**3c**) from a detailed consideration of spectroscopic data. By contrast, prolonged stirring (7 days) of $[Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**2b**) in thf affords mononuclear $[Mo(C{=}CHBu^t)(dppe)(\eta\text{-}C_7H_7)]^+$ (**4b**) as the major product, identified by comparison of ^1H NMR data with those for an authentic sample prepared by protonation of **1b**. Presumably in this latter example dimerisation is blocked sterically, and formation of **4b** proceeds via hydrogen radical abstraction from the solvent.

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* CHO is the centroid of the cycloheptatrienyl ring.