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Cyclic oxacarbene complexes of the cycloheptatrienylmolybdenum auxiliary $MoL_2(\eta\text{-}C_7H_7)$, L = CO or P-donor ligand: isolation and subsequent cyclisation of a hydroxyvinylidene intermediate

Roy L. Beddoes, Richard W. Grime, Zafar I. Hussain and Mark W. Whiteley *

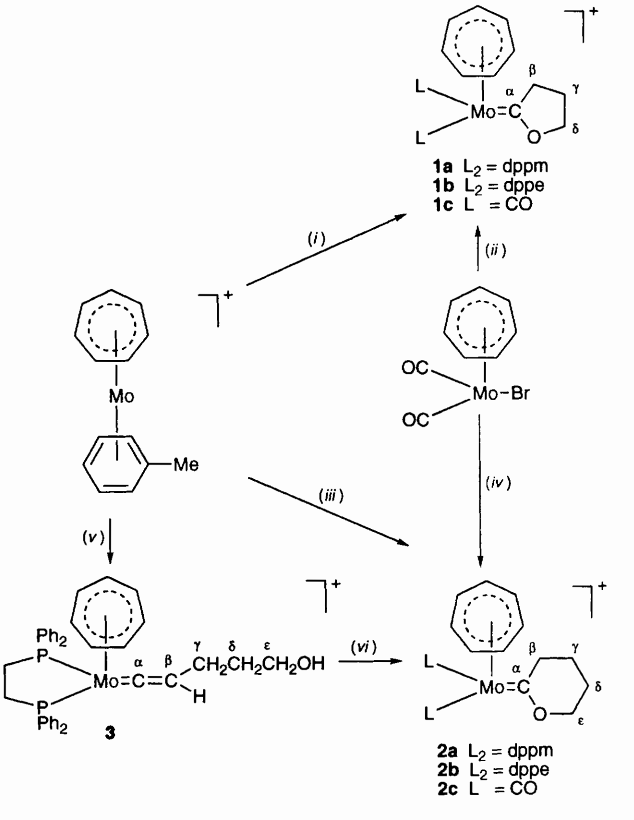
Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

The cyclic oxacarbene complexes $[Mo\{\overline{CCH_2(CH_2)_nCH_2O}\}L_2(\eta\text{-}C_7H_7)]PF_6$ [$n = 1$ or 2; L = CO, $L_2 = Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$ (dppe)] have been synthesised and the 1-oxacyclopent-2-ylidene ligand in the derivative $n = 1$, L_2 = dppe shown to adopt a horizontal orientation; the crystallographically characterised, hydroxyvinylidene complex $[Mo\{C{=}C(H)CH_2CH_2CH_2OH\}(dppe)(\eta\text{-}C_7H_7)]PF_6$ is an isolable intermediate in the formation of $[Mo\{\overline{CCH_2(CH_2)_2CH_2O}\}(dppe)(\eta\text{-}C_7H_7)]PF_6$.

The cycloheptatrienylmolybdenum auxiliary $MoL_2(\eta\text{-}C_7H_7)$ (L = CO or P-donor ligand) [1] presents an interesting alternative to the commonly employed $ML_2(\eta\text{-}L')$ (M = Fe or Ru; L′ = C_5H_5, C_5Me_5 *etc.*) systems as an agent to effect metal-assisted organic transformations but, with the exception of our investigations [2–4] on vinylidene and alkynyl derivatives, the potential of this chemistry awaits exploitation. The work presented here demonstrates the capacity of the $MoL_2(\eta\text{-}C_7H_7)$ auxiliary to induce novel structure and reactivity into the cyclic oxacarbene complexes $[Mo\{\overline{CCH_2(CH_2)_nCH_2O}\}L_2(\eta\text{-}C_7H_7)]^+$ [$n = 1$ or 2; L = CO, $L_2 = Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PCH_2CH_2PPh_2$ (dppe)].

Although alkoxy-carbene complexes $[Mo\{C(OR')R''\}L_2(\eta\text{-}C_7H_7)]^+$ (R′ = alkyl, R″ = alkyl or Ph) are not accessible by reaction of alcohols R′OH with suitable cationic vinylidene precursors, the cyclic oxacarbene complexes $[Mo\{\overline{CCH_2(CH_2)_nCH_2O}\}L_2(\eta\text{-}C_7H_7)]PF_6$ [$n = 1$, L_2 = dppm **1a**, dppe **1b**, L = CO **1c**; $n = 2$, L_2 = dppm **2a**, L = CO **2c**: Scheme 1] have been obtained by reaction of hydroxyalk-1-ynes with either (*i*) $[Mo(OCMe_2)L_2(\eta\text{-}C_7H_7)]PF_6$ {generated *in situ* from $[Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]PF_6$ and L_2 in refluxing acetone, L_2 = dppm or dppe}, or (*ii*) $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$–$NH_4PF_6$ in methanol. Spectroscopic data † for the new complexes confirm their identity as carbene derivatives with characteristic low field shifts for C_α (δ in the range 330–345) in the $^{13}C\text{-}\{^1H\}$ NMR spectra. These complexes, together with $[Mo(\overline{CCH_2CH_2CH_2O})(CO)L(\eta\text{-}C_7H_7)]^+$ (L = PPh_3 or PMe_3),[3] are the only examples of carbene derivatives of any cycloheptatrienyl metal system and their syntheses demonstrate the ability of the $MoL_2(\eta\text{-}C_7H_7)$ auxiliary to effect hydroxyalk-1-yne to cyclic carbene transformations with a range of supporting ligands L, which impart a wide variation in electron density at the Mo centre.

A key objective driving the synthesis of carbene derivatives of a symmetrical $MoL_2(\eta\text{-}C_7H_7)$ auxiliary was to determine the carbene ligand orientation. Ligands CR_2, $C{=}CR_2$ *etc.* with R substituents which lie in the pseudo-mirror plane of the



Scheme 1 Yields (%) in parentheses. (*i*) L_2 = dppm or dppe, reflux in acetone 18 h then $HC{\equiv}CCH_2CH_2OH$ reflux in acetone 3 h, **1a** (53), **1b** (73) from $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]PF_6$ (1.46 g), dppe (1.37 g) and $HC{\equiv}CCH_2CH_2OH$ (0.80 g); (*ii*) $HC{\equiv}CCH_2CH_2OH$–NH_4PF_6, reflux in methanol 2 h, **1c** (37) from $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ (0.59 g), NH_4PF_6 (0.45 g) and $HC{\equiv}CCH_2CH_2OH$ (0.40 g); (*iii*) L_2 = dppm, reflux in acetone 18 h, then $HC{\equiv}CCH_2CH_2CH_2OH$ reflux in acetone 2 h, **2a** (9); (*iv*) $HC{\equiv}CCH_2CH_2CH_2OH$–$NH_4PF_6$, reflux in methanol 40 min, **2c** (19); (*v*) L_2 = dppe, reflux in acetone 18 h, then $HC{\equiv}CCH_2CH_2CH_2OH$ reflux in acetone 30 min, **3** (31) from $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]PF_6$ (0.50 g), dppe (0.50 g) and $HC{\equiv}CCH_2CH_2CH_2OH$ (0.40 g); (*vi*) reflux in methanol 18 h, **2b** (43), or LiCl reflux in acetone 18 h, **2b** (16) from **3** (0.34 g) and LiCl (0.002 g)

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† Selected spectroscopic data (lettering as in Scheme 1, t = triplet, m = multiplet, br = broad): **1b**, ^1H NMR [$(CD_3)_2CO$], δ 7.91–7.62 (20 H, Ph), 5.27 (t, 7 H, C_7H_7), 4.06 (t, 2 H, H_δ), 2.69 (t, 2 H, H_β), 2.39 (m, 4 H, CH_2 of dppe) and 1.46 (m, 2 H, H_γ); ^{13}C NMR (CD_2Cl_2), δ 331.7 [t, *J*(P–C) 18 Hz, C_α], 137.2–129.4 (Ph), 89.6 (C_7H_7), 82.3 (C_δ), 57.2 (C_β), 27.9 (CH_2 of dppe) and 23.3 (C_γ); **2b**, ^1H NMR [$(CD_3)_2CO$], δ 8.00–7.60 (20 H, Ph), 5.34 (t, 7 H, C_7H_7), 3.76 (t, 2 H, H_ε), 2.69 (t, 2 H, H_β), 2.37 (m, 4 H, CH_2 of dppe), 1.46 (m, 2 H, H_δ) and 1.10 (m, 2 H, H_γ); ^{13}C NMR [$(CD_3)_2CO$], δ 342.6 [t, *J*(P–C) 18 Hz, C_α], 137.9–129.5 (Ph), 89.8 (C_7H_7), 72.0 (C_ε), 47.8 (C_β), 28.2 (CH_2 of dppe), 21.3 (C_δ) and 17.0 (C_γ); **1c**, IR (CH_2Cl_2) 2037, 1997 cm^{-1} ν(CO); ^1H NMR (CD_2Cl_2), δ 5.73 (7 H, C_7H_7), 5.07 (t, 2 H, H_δ), 3.67 (t, 2 H, H_β) and 2.08 (m, 2 H, H_γ); ^{13}C NMR (CD_2Cl_2), δ 332.6 (C_α), 208.1 (CO), 96.9 (C_7H_7), 89.0 (C_δ), 62.4 (C_β) and 21.6 (C_γ); **3**, ^1H NMR (CD_3CN), δ 7.84–7.29 (20 H, Ph), 5.20 (br, 7 H, C_7H_7), 4.38 (br, 1 H, H_β), 3.12 (2 H, H_ε), 2.54, 2.42 (m, 4 H, CH_2 of dppe), 1.37 (br, 2 H) and 1.04 (br, 2 H, H_γ and H_δ); ^{13}C NMR (CD_3CN), δ 133.9–128.6 (Ph), 115.3 (C_β), 91.5 (C_7H_7), 60.5 (C_ε), 31.6 and 22.3 (C_γ and C_δ) and 26.0 (CH_2 of dppe). Satisfactory microanalyses (C, H, N) were obtained for all new complexes reported.

$MoL_2(\eta\text{-}C_7H_7)$ moiety possess a 'vertical' orientation, whilst ligands with R substituents located orthogonal to this plane are termed 'horizontal'. Our recent observation of a vertically orientated vinylidene ligand in $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)]BF_4$ suggested that $Mo(dppe)(\eta\text{-}C_7H_7)$ might promote electronically preferred ligand orientations which are the converse of those supported by the $RuL_2(\eta\text{-}C_5H_5)$ auxiliary.[4] Further to establish this hypothesis, the purpose of the current work was to extend these comparisons to carbene ligands. The crystal structure* of the 1-oxacyclopent-2-ylidene complex $[Mo(\overline{CCH_2CH_2CH_2O})(dppe)(\eta\text{-}C_7H_7)]PF_6\cdot 0.5CH_2Cl_2$ reveals two crystallographically distinct cations A and B differing principally in the carbene ligand conformation; in molecule A (Fig. 1) the non-hydrogen atoms of the carbene ligand are essentially coplanar whilst in B an envelope conformation is adopted. The $Mo\text{–}C_\alpha$ bond distances [A 2.04(3) and B 2.02(3) Å] are intermediate between those of the formal Mo–C single bond of $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$ [2.244(9) Å][6] and the vinylidene $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)]BF_4$ [$Mo\text{–}C_\alpha$ 1.93(1) Å]. However the salient structural feature of both A and B is the horizontal orientation of the oxacarbene ligand which consistent with theoretical investigations[7] is twisted through approximately 90° from the vertical orientation of the vinylidene ligand in $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)]BF_4$ and moreover is diametrically opposite to that of the *anti*-periplanar, vertical arrangement of the oxacarbene ligand in $[Ru(\overline{CCH_2CH_2CH_2O})(dppe)(\eta\text{-}C_5H_5)]PF_6$.[8] The contrasting ligand orientation preferences of $MoL_2(\eta\text{-}C_7H_7)$ and $RuL_2(\eta\text{-}C_5H_5)$ auxiliaries are therefore confirmed for both carbene and vinylidene ligands and these findings anticipate the prospect of metal auxiliary dependent, stereochemical control.

It has long been assumed that the formation of cyclic oxacarbene complexes from hydroxyalk-1-ynes proceeds *via* intramolecular cyclisation of a hydroxyvinylidene intermediate[9–11] but there is little direct evidence to support such a mechanism.[12] However, when a solution of $[Mo(OCMe_2)(dppe)(\eta\text{-}C_7H_7)]PF_6$ in refluxing acetone was treated with pent-4-yn-1-ol, unexpectedly, and in contrast to the formation of carbene **2a** by the analogous dppm system, the isolated product was the hydroxyvinylidene $[Mo\{C{=}C(H)CH_2CH_2CH_2OH\}(dppe)(\eta\text{-}C_7H_7)]PF_6$ **3**. The identity of **3** was suggested by spectroscopic data† and was subsequently confirmed by a crystal-structure determination.* The molecular configuration of **3** (Fig. 2) reveals a *syn*-periplanar, vertically orientated hydroxyvinylidene ligand with the more sterically demanding $CH_2CH_2CH_2OH$ substituent directed 'up' towards the cycloheptatrienyl ring; these structural features are in accord with those of $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)]BF_4$.[4] The existence of the 1-oxacyclohex-2-ylidene, dppm complex **2a**, suggested that, under appropriate conditions, the dppe analogue **2b** might also be accessible starting from **3**. Two procedures were developed to effect conversion of **3** into **2b** involving either reflux of a solution of **3** in methanol or

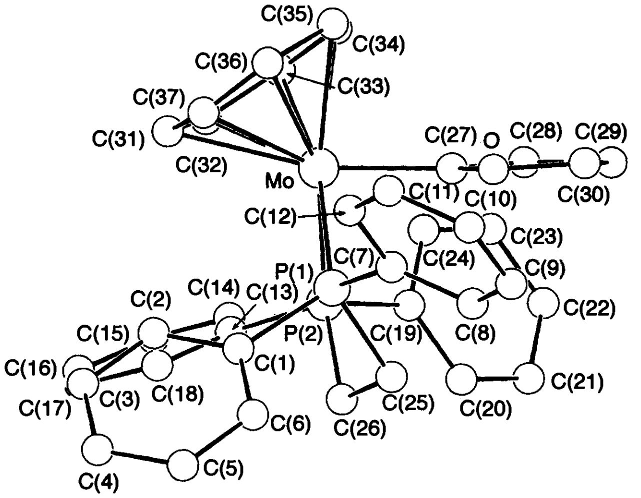

Fig. 1 Molecular structure of complex **1b**, hydrogen atoms and PF_6 counter anion omitted. Important bond lengths (Å) and angles (°): Mo–C(27) 2.04(3), Mo–P(1) 2.515(8), Mo–P(2) 2.515(7), C(27)–O 1.32(4); P(1)–Mo–P(2) 77.8(2), P(1)–Mo–C(27) 82.9(8), P(2)–Mo–C(27) 89.5(7), Ct–Mo–C(27) 125, dihedral angle between planes {Ct–Mo–C(27)} and {C(28)–C(27)–O} 85° (Ct ≡ C_7H_7 ring centroid)

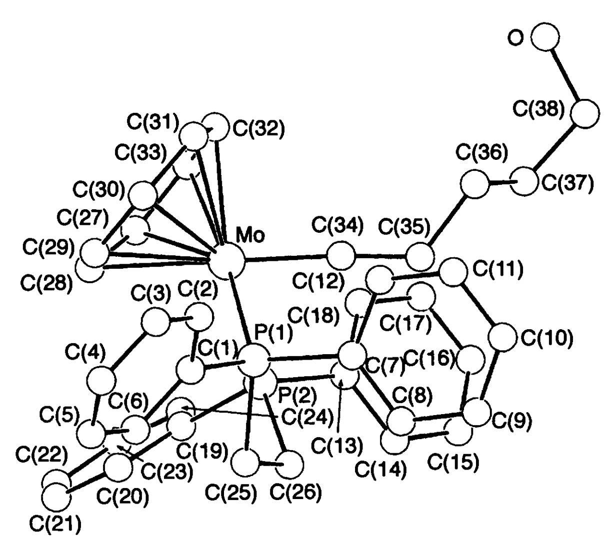

Fig. 2 Molecular structure of complex **3**, hydrogen atoms and PF_6 counter anion omitted. Important bond lengths (Å) and angles (°): Mo–C(34) 1.91(1), Mo–P(1) 2.515(3), Mo–P(2) 2.501(3), C(34)–C(35) 1.31(1); P(1)–Mo–P(2) 81.26(9), P(1)–Mo–C(34) 82.2(3), P(2)–Mo–C(27) 78.8(3), Mo–C(34)–C(35) 176(1), C(34)–C(35)–C(36) 126(1), Ct–Mo–C(34) 136, dihedral angle between planes {Ct–Mo–C(34)} and {C(34)–C(35)–C(36)} 6° (Ct ≡ C_7H_7 ring centroid)

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* Crystal data. **1b**: $C_{37.5}H_{38}ClF_6MoOP_3$, $M = 843.02$, crystal dimensions 0.01 × 0.17 × 0.35 mm, $a = 9.919(4)$, $b = 44.23(2)$, $c = 17.402(5)$ Å, $\beta = 104.64(3)°$, $U = 7387(4)$ Å^3, $Z = 8$, $D_c = 1.516$ g cm^{-3}, $F(000) = 3432$, μ(Cu-Kα) 54.22 cm^{-1}, Lorentz, polarisation and absorption corrections applied, transmission factors 0.79 to 1.11, 2959 reflections with $I > 3.00\sigma(I)$ used in refinement. The asymmetric unit incorporates two crystallographically distinct cations, two PF_6^- counter ions and one CH_2Cl_2 solvent molecule and this large unit, coupled with weak crystal diffracting power resulted in relatively poor quality final data. Solution by direct methods; carbon and fluorine atoms refined isotropically, other non-hydrogen atoms anisotropically, hydrogen atoms included in idealised positions (C–H 0.95 Å) and assigned isotropic thermal parameters 20% greater than the equivalent *B* value of the atom to which they were bonded; phenyls and hexafluorophosphates refined as rigid groups. $(\Delta\rho)_{max} = 0.88$, $(\Delta\rho)_{min} = -0.65$ e Å^{-3}, $R = 0.081$, $R' = 0.103$.

3: $C_{38}H_{39}F_6MoOP_3$, $M = 814.58$, crystal dimensions 0.05 × 0.25 × 0.25 mm, $a = 8.912(4)$, $b = 20.366(9)$, $c = 19.713(6)$ Å, $\beta = 91.62(3)°$, $U = 3576(3)$ Å^3, $Z = 4$, $D_c = 1.513$ g cm^{-3}, $F(000) = 1664$, μ(Cu-Kα) 48.85 cm^{-1}, Lorentz, polarisation and absorption corrections applied, transmission factors 0.78 to 1.19, 3400 reflections with $I > 3.00\sigma(I)$ used in refinement. Solution by direct methods; non-hydrogen atoms refined anisotropically, hydrogen atoms located by Fourier-difference methods and then set (except OH) to idealised positions (C–H 0.95 Å) and assigned isotropic thermal parameters 20% greater than the equivalent *B* value of the atom to which they were bonded. $(\Delta\rho)_{max} = 0.61$, $(\Delta\rho)_{min} = -0.83$ e Å^{-3}, $R = 0.068$, $R' = 0.081$.

Data common to **1b** and **3**. Rigaku AFC5R diffractometer, Cu-Kα radiation (λ = 1.541 78 Å), monoclinic, space group $P2_1/n$ (no. 14). Calculations were performed using the TEXSAN crystallographic software packages of Molecular Structure Corporation[5] with refinements based on *F*. Weighting scheme employed: $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/228.

alternatively reflux in acetone in the presence of LiCl. Both methods gave a mixture of $[\mathrm{Mo}\{\overline{\mathrm{CCH_2(CH_2)_2CH_2O}}\}(\mathrm{dppe})(\eta\text{-}\mathrm{C_7H_7})]^+$ **2b** and unreacted **3** which were then separated by fractional recrystallisation. This transformation of an isolable hydroxyvinylidene to a cyclic oxacarbene complex is without precedent and yet further establishes the novel chemistry of the $\mathrm{MoL_2}(\eta\text{-}\mathrm{C_7H_7})$ auxiliary.

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