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A mercury bis(tricarbido) complex: $[Hg\{C\equiv C–C\equiv W(CO)_2Tp\}_2(dmso)_4](dmso)_2$ (Tp = hydrotrispyrazolylborate)

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Fluoride mediated desilylation of the propargylidyne complex $[W(\equiv C–C\equiv CSiMe_3)(CO)_2\{HB(pz)_3\}]$ (pz = pyrazol-1-yl) in the presence of mercury(II) chloride provides the novel bis(tricarbido)complex $[Hg\{C\equiv C–C\equiv W(CO)_2\{HB(pz)_3\}\}_2]$, which was structurally characterised as a dmso hexasolvate.

Bis(alkynyl)mercurials, $Hg(C\equiv CR)_2$, have a long history. Numerous examples have been isolated, primarily as an early method for the characterisation of terminal alkynes by conversion to crystalline derivatives.[1] In the interim they have served as air and moisture stable transalkynylating agents for the synthesis of alkynyls of transition metals,[2] lanthanides[3] and main group elements.[4] Our interest in these reagents centres on their catalytic demercuration to provide 1,3-diynes and as precursors to σ-enynyl complexes.[5] An intriguing aspect of these compounds to emerge only recently is their association in the solid state *via* Hg···Hg interactions reminiscent of aurophilic associations.[6] We have recently been concerned with the development of new synthetic routes to tricarbido complexes,[7] *i.e.*, compounds in which two metals are linked by a three-carbon bridge (Fig. 1).[8] Prior to this, such complexes were limited to the original examples provided by Gladysz[9] and Templeton,[10] which whilst establishing the class of compound, were arrived at by elegant but non-general synthetic routes. Our perspective was to view propargylidyne complexes $L_nM\equiv C–C\equiv CR$[11,12] as potential synthons for the C_3 unit. Towards this end we found that fluoride mediated protodesilylation of a range of silylpropargylidynes provided access, *in situ*, to the parent complexes $L_nM\equiv C–C\equiv CH$ or their conjugate bases. However each of these classes of intermediate have so far eluded isolation. We have therefore turned our attention to the synthesis of mercury bis(tricarbido) compounds in the hope that as for alkynyl mercurials, they will provide isolable and convenient reagents for developing tricarbido chemistry.

The reaction of $[W(\equiv C–C\equiv CSiMe_3)(CO)_2\{HB(pz)_3\}]$, **1a**,[12] in dichloromethane with $[^nBu_4N]F$ ('TBAF') in the presence of half an equivalent of mercuric chloride provides a red–purple compound that is formulated as the trimetallic complex $[Hg\{C\equiv C–C\equiv W(CO)_2\{HB(pz)_3\}\}_2]$, **2a**, on the basis of spectroscopic and microanalytical data (Scheme 1).† In a similar manner the more sterically encumbered complex $[W(\equiv C–C\equiv CSiMe_3)(CO)_2\{HB(pz')_3\}]$ (pz′ = 3,5-dimethylpyrazol-1-yl), **1b**,[12] may be converted to the trimetallic complex $[Hg\{C\equiv C–C\equiv W(CO)_2\{HB(pz')_3\}\}_2]$, **2b**.†

Spectroscopic data for the two complexes are comparable and so only those for **2a** will be discussed. The complex **2a** has somewhat limited solubility in common organic solvents requiring the use of dmso for the acquisition of NMR data, a choice which nevertheless proved fortuitous (*vide infra*). Spectroscopic data of note include resonances in the $^{13}C\{^1H\}$ NMR spectrum at δ = 253.6, 120.6 and 104.2 which are assigned to C_α, C_β and C_γ of the C_3 bridges. The alkynyl groups give rise to a weak infrared absorption at 2047 cm^{-1} (CH_2Cl_2), whilst replacement of silicon in **1a** by mercury in **2a** does not give rise to a discernable shift in the frequencies of the carbonyl ligands.

Although we failed to obtain crystals of either **2a** or **2b** from a range of solvents, prolonged storage of a solution of **2b** in d_6-dmso resulted in the deposition of crystals of the solvate **2a**·$(dmso)_6$. The results of a crystallographic analysis are summarised in Fig. 2. For comparative purposes the precursor **1a** was also structurally characterised and the results of that study are summarised in Fig. 3. The molecular geometry of **2a** involves a linear arrangement of the two WC_3 'ligands' about the central mercury atom, which lies on an inversion centre such that only half the molecule is unique. The coordination number of mercury is increased to six by the weak association of four dmso molecules with Hg–O separations of 2.937(4) and 2.986(6) Å. Comparatively few structural data are available for mercury alkynyls and interpretation can be clouded by aggregation for base-free examples $[Hg(C\equiv CR)_2]$ which have Hg–C separations of 2.009–2.017 Å (R=Ph) and 1.976–2.032 Å ($R=SiMe_3$).[6] Mercury alkynyls show weak Lewis acidic character as illustrated by the structurally characterised complex $[Hg(C\equiv CPh)_2(o\text{-phen})]$[13] which retains an essentially linear C–Hg–C arrangement with Hg–C bonds of 2.031 and 2.047 Å. Thus for **2a**, the Hg–C3 bond length of 2.020(5) Å appears unremarkable, despite the mercury being six coordinate. Bond lengths along the WC_3Hg chain reflect a localised W≡C1–C2≡C3–Hg valence bond description. Thus W–C1, C1–C2 and C2–C3 bond lengths of 1.849(5), 1.365(7) and 1.216(7) Å, respectively, may be compared with 1.844(6), 1.366(8) and 1.236(9) Å found for the precursor complex **1a** (Fig. 1). The angle at C3 is essentially linear (176.5(5)°) in contrast to the unusually distorted mercury bis(tetracarbido) complex $[Hg\{C_4Ru(dppe)(\eta\text{-}C_5Me_5)\}_2]$ reported recently by Bruce.[14] We note that **2a**·$(dmso)_6$ is the first example of a structurally characterised six co-ordinate diorganomercurial 'HgR_2L_4' with unidentate ligands.

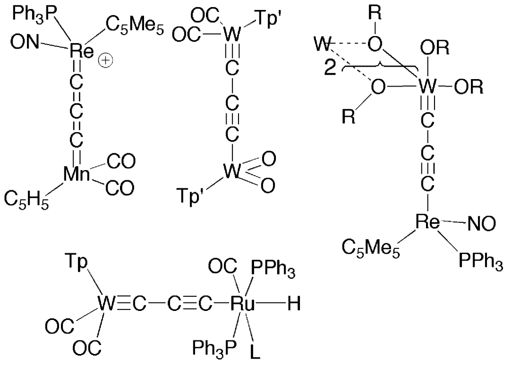
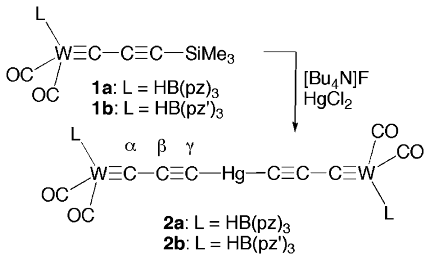


Fig. 1 Tricarbido complexes. Tp = $HB(pz)_3$, Tp′ = $HB(pz')_3$. L = CO, PPh_3, Hpz′, $CNC_6H_3Me_2$-2,6.



Scheme 1 Synthesis of **2**.

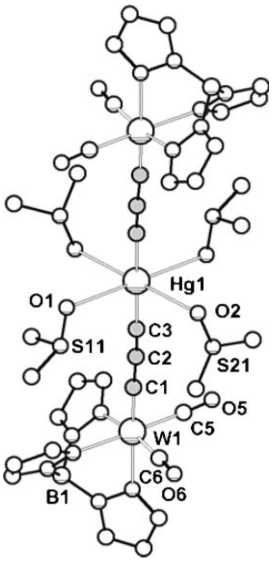


Fig. 2 Molecular geometry of **2a**·(dmso)$_6$ in the crystal (lattice dmso molecules and hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Hg1–O1 2.937(4), Hg1–O2 2.986(6), Hg1–C3 2.020(5), W1–N11 2.267(4), W1–N21 2.210(4), W1–N31 2.202(4), W1–C1 1.849(5), W1–C5 2.009(6), W1–C6 1.984(6), C1–C2 1.365(7), C2–C3 1.216(7), O1^i–Hg1–O2 82.4(2), O1^i–Hg1–C3 93.2(2) O2^i–Hg1–C3 93.5(2), O1–Hg1–O2 97.6(2), O1–Hg1–C3 86.8(2), O2–Hg1–C3 86.5(2), N21–W1–C1 97.6(2), N31–W1–C1 104.4(2), C1–W1–C5 87.3(2), C1–W1–C6 85.2(2), W1–C1–C2 174.9(4), C1–C2–C3 178.0(6), C2–C3–Hg1 176.5(5).

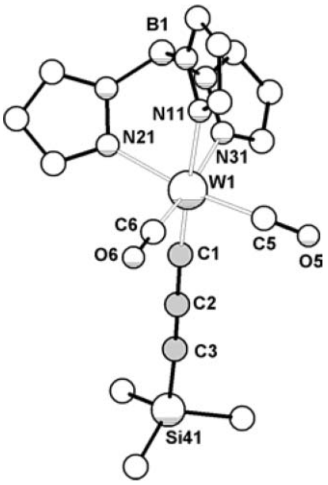


Fig. 3 Molecular geometry of **1a** in the crystal (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): W1–N11 2.268(4), W1–N21 2.202(4), W1–N31 2.191(4) W1–C1 1.844(6), W1–C5 1.975(7), W1–C6 1.986(6), C1–C2 1.366(8), C2–C3 1.236(9), N11–W1–N31 80.7(2), N21–W1–N31 81.4(2), N21–W1–C1 100.7(2), N31–W1–C1 98.8(2), N11–W1–C5 90.3(2), C1–W1–C5 88.1(3), N11–W1–C6 91.8(2), W1–C1–C2 176.4(5), C1–C2–C3 178.6(7).

Notes and references

† Selected characterisational data: **2a**: Yield 49%. IR (CH_2Cl_2): 2047 [ν(C≡C)], 1992, 1905 [ν(W–CO)] cm^{-1}. NMR ^{1}H (DMSO, 25 °C): δ 8.02 [d, 4 H, $^3J_{HH}$ = 1.8 Hz, H^3], 7.97 [d, 4 H, $^3J_{HH}$ = 2.1 Hz, H^5], 7.95 [d, 2 H, $^3J_{HH}$ = 2.3 Hz, H^3], 7.80 [d, 2 H, $^3J_{HH}$ = 2.0 Hz, H^5], 6.40 [t, 4 H, $^3J_{HH}$ = 2.3 Hz, H^4], 6.28 [d, 2 H, $^3J_{HH}$ = 2.2 Hz, H^4] ppm. ^{13}C{^{1}H} (DMSO, 25 °C): δ 253.6 [W≡C], 225.8 [W–CO], 145.1 (2 C), 144.2 (1 C) [C^5(pz)], 136.6 (3 C) [C^3(pz)], 120.6 [*C*≡C–Hg] 106.7 (3 C) [C^4(pz)], 104.2 [C≡*C*–Hg] ppm. MS (ESI): *m*/*z* 1179 [M]$^+$. Anal. Found: C 28.92, H 1.99, N 13.73. Calcd. for $C_{28}H_{20}B_2HgN_{12}O_4W_2$: C 28.54, H 1.71, N 14.26. **2b**: Yield 57%. IR (CH_2Cl_2): 2042 [ν(C≡C)], 1983, 1895 [ν(W–CO)] cm^{-1}. NMR ^{1}H ($CDCl_3$, 25 °C): δ 5.89 [s, 4 H, H^4], 5.72 [s, 2 H, H^4], 2.54 [s, 6 H, C^{3}CH$_3$], 2.35 [s, 9 H, C^{5}CH$_3$], 2.29 [s, 3 H, C^{3}CH$_3$] ppm. ^{13}C{^{1}H} ($CDCl_3$, 25 °C): δ 246.7 [W≡C], 225.6 [s + d, $^1J_{CW}$ = 171 Hz, W–CO], 152.3 (1 C), 152.2 (2 C) [C^5(pz)], 145.2 (1 C), 144.5 (2 C) [C^3(pz)], 120.5 [*C*≡C–Hg], 106.6 (1 C), 106.6 (2 C) [C^4(pz)], 106.4 [C≡*C*–Hg], 16.4 (2 C), 15.2 (1 C) [C^{3}Me(pz)], 12.6 [C^{5}Me(pz)] ppm. Crystal data for **1a**: $C_{17}H_{19}BN_6O_2SiW$, $M = 562.12$, trigonal, $R\bar{3}$ $a = b = 38.1017(5)$, $c = 8.1896(1)$ Å, $V = 10296.3(2)$ Å^3, $Z = 18$, $\rho_{calc} = 1.632$ gcm^{-3}, μ(Mo Kα) = 5.123 mm^{-1}, $T = 200$ K, red prism, 5264 independent measured reflections ($2\theta \leqslant 55°$), $R = 0.027$, $wR = 0.028$ for 2881 independent observed absorption-corrected reflections [$I > 3\sigma(I)$], 251 parameters. CCDC 245028. Crystal data for **2a**·(dmso)$_6$: $C_{28}H_{20}B_2HgN_{12}O_4W_2.(Me_2SO)_6$, $M = 1647.27$, triclinic, $P\bar{1}$, $a = 9.3324(2)$, $b = 12.4640(2)$, $c = 13.5127(2)$ Å, $\alpha = 66.7946(8)$, $\beta = 84.4796(7)$, $\gamma = 86.4672(8)°$, $V = 1437.44(4)$ Å^3, $Z = 1$, $\rho_{calc} = 1.903$ gcm^{-3}, μ(Mo Kα) = 6.933 mm^{-1}, $T = 200$ K, orange plate, 6594 independent measured reflections ($2\theta \leqslant 55°$), $R = 0.026$, $wR = 0.029$ for 4582 independent observed absorption-corrected reflections [$I > 3\sigma(I)$], 337 parameters. CCDC 245028, 245029. See http://www.rsc.org/suppdata/cc/b4/b412972e/ for crystallographic data in .cif or other electronic format.

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