Syntheses of metal diynyl complexes: novel routes to all-carbon ligands

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CuI-catalysed reactions between halide complexes of Fe, Mo, W or Pt and an excess of buta-1,3-diyne in the presence of diethylamine lead to the formation of buta-1,3-diynyl compounds; elaboration of the diynyl ligand is achieved by replacement of H by either non-metal or metal groups, by coordination to the C≡C triple bonds and by incorporation of the terminal C atoms into clusters with consequent electronic rearrangement along the C_4 chain.

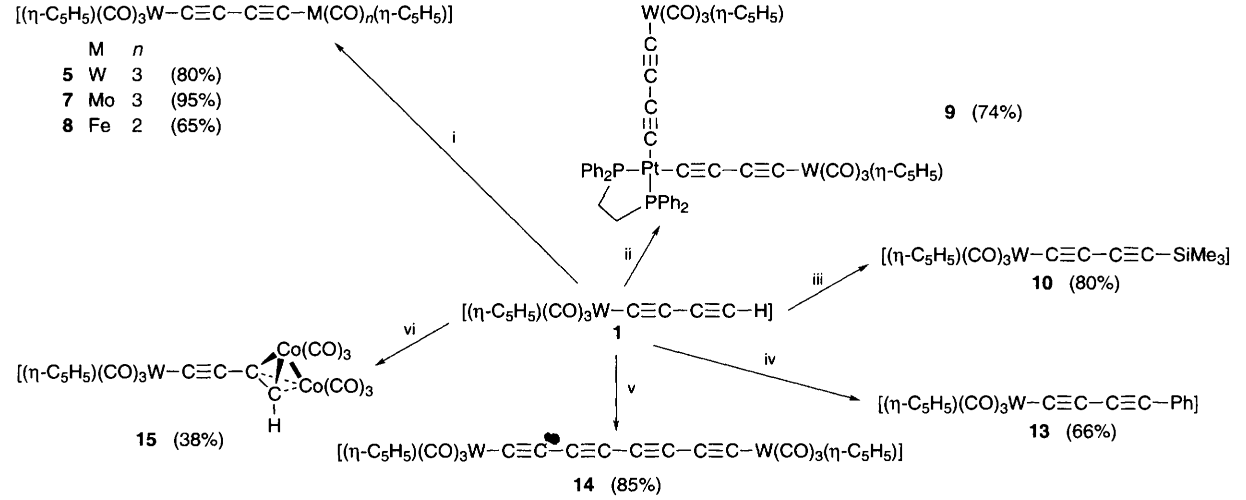
As part of our studies on the properties of metal complexes and clusters containing all-carbon ligands,[1] we required access to a number of transition-metal-substituted diacetylides. Bimetallic compounds with carbon bridges linking the metal centres, $[L_mM]–C_n–[M'L'_m]$, also excite interest because of their potential applications in the new materials industry.[2] Several synthetic routes to diynyl complexes have been reported.[3] However, the preparation of asymmetrically substituted diacetylides using existing methodologies generally requires either a multi-step protection/deprotection approach,[3b,d,e,h] or the preparation of a terminal diyne, HC≡CC≡CR, for each diacetylide complex desired.[3f] We now report simple procedures that yield a range of (*i*) metal–diynyl complexes bearing the C≡CC≡CH ligand; (*ii*) novel homo- and hetero-bimetallic C_4 complexes; (*iii*) substituted derivatives of general form $[W(C{\equiv}CC{\equiv}CR)(CO)_3(\eta\text{-}C_5H_5)]$ (R = $SiMe_3$, Ph, PPh_2); (*iv*) new heterometallic clusters containing $\mu_3,\eta^1:\mu_3,\eta^1$-CC≡CC ligands, using buta-1,3-diyne as the only source of the C_4 ligand.

A useful general synthesis of transition-metal acetylide complexes is from CuI-catalysed reactions of the halides with alk-1-ynes in amine solvents.[4] Similar preparations of group 10 diynyl complexes were reported by Hagihara and coworkers some years ago.[3b] These reactions have now proved to be excellent sources of diynyl complexes containing a range of different metals. For example, addition of a five-fold excess of buta-1,3-diyne, as a 2 mol dm^{-3} solution in thf,[5] to an $NHEt_2$ solution of $[WCl(CO)_3(\eta\text{-}C_5H_5)]$ in the presence of CuI resulted in a rapid colour change from red to bright yellow, and the precipitation of $[NH_2Et_2]Cl$. The complex $[W(C{\equiv}CC{\equiv}CH)(CO)_3(\eta\text{-}C_5H_5)]$ **1** (Scheme 1) was isolated as a bright yellow powder (90%) after column chromatography on Al_2O_3.† Similar reactions with, for example, $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$, $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ and $[PtCl_2(dppe)]$, gave $[Mo(C{\equiv}CC{\equiv}CH)(CO)_3(\eta\text{-}C_5H_5)]$ **2** (60%), $[Fe(C{\equiv}CC{\equiv}CH)(CO)_2(\eta\text{-}C_5H_5)]$ **3** (30%)[3b,e] and $[Pt(C{\equiv}CC{\equiv}CH)_2(dppe)]$ **4** (94%), respectively.

The diynediyl complexes are each characterised by a single, strong ν(C≡C) absorption near 2150 cm^{-1}, while in their ^{13}C NMR spectra, resonances near δ 110, 72, 70 and 65 were assigned to C_α, C_β, C_γ and C_δ, respectively. For **1**, and the other W diynyl complexes described below, C_α showed coupling to ^{183}W (J_{CW} typically 60–70 Hz). The C_β and C_γ carbons of **1** also displayed longer-range coupling to ^{183}W, which assisted in their assignment. The reactivity of the free C≡CH group in **1**–**4** has been examined, resulting in the formation of a variety of complexes containing di- and poly-alkynyl ligands. Representative examples for **1** are shown in Scheme 1 and described below. In general, the terminal alkyne moiety behaves as a typical, if rather electron-rich, organic acetylene.

Replacement of the acetylenic H atom in **1** is readily achieved. For example, addition of an equimolar amount of $[WCl(CO)_3(\eta\text{-}C_5H_5)]$ to a solution of **1** in thf–$NHEt_2$ containing a catalytic amount of CuI resulted in the formation of the bis-metallated diynediyl complex $[\{(\eta\text{-}C_5H_5)(CO)_3W\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)]$ **5** (80%) as a rather insoluble yellow powder.† The Mo analogue **6** (77%) and the heterobimetallic complexes $\{(\eta\text{-}C_5H_5)(CO)_3W\}C{\equiv}CC{\equiv}C\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$ **7** (95%), $[\{(\eta\text{-}C_5H_5)(CO)_3W\}C{\equiv}CC{\equiv}C\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ **8** (65%)[3b] and $[Pt\{C{\equiv}CC{\equiv}C[W(CO)_3(\eta\text{-}C_5H_5)]\}_2(dppe)]$ **9** (74%) were prepared using the same methodology with the appropriate chloro-metal precursors.

Whilst attempts to react **1** with Bu^nLi resulted in extensive decomposition, **1** is cleanly deprotonated by lithium diisopropylamide and the resulting anion can be trapped by reactions



Scheme 1 *Reagents*: i, CuI, $NHEt_2$, $[ML_n]Cl$; ii, CuI, $NHEt_2$, $[PtCl_2(dppe)]$; iii, LDA, $SiClMe_3$; iv, C_6H_5I, $[Pd(PPh_3)_4]$, CuI; v, $[Cu(tmeda)]Cl$, O_2; vi, $[Co_2(CO)_8]$. Yields in parentheses.

with $SiClMe_3$, $PClPh_2$ or $[MnBr(CO)_5]$ to give $[W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3(\eta\text{-}C_5H_5)]$ **10** (80%), $[W(C{\equiv}CC{\equiv}CPPh_2)(CO)_3(\eta\text{-}C_5H_5)]$ **11** (25%) and $[\{(\eta\text{-}C_5H_5)(CO)_3W\}C{\equiv}CC{\equiv}C\{Mn(CO)_5\}]$ **12** (20%), respectively.

The terminal diynyl ligand can be coupled with iodoarenes in the presence of catalytic amounts of $[Pd(PPh_3)_4]$ and CuI. Thus $[W(C{\equiv}CC{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)]$ **13**† was prepared in 66% yield by treating a diisopropylamine solution of **1** with a 1.5-fold excess of iodobenzene in the presence of the mixed catalyst. Similar reactions with *p*-iodoanisole, *p*-iodotoluene and methyl *p*-iodobenzoate yielded the substituted derivatives in 35–90% yields.

Recently, the dimetallated tetraynes $[\{Re(PPh_3)(NO)(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}C_8)]$[6] and $[\{Fe(dppe)(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}C_8)]$[7] have been prepared by oxidative coupling of the appropriate diynyl complexes using $Cu(O_2CMe)_2$ in pyridine at elevated temperatures. Similar attempts to prepare $[\{(\eta\text{-}C_5H_5)(CO)_3W\}_2(\mu\text{-}C_8)]$ **14** resulted only in extensive decomposition of **1**. However, under the milder Hay conditions (Cu_2Cl_2–tmeda, O_2 purge, acetone, room temp.),[8] homo-coupling of the diynyl ligand proceeded smoothly to give the dimetallated tetrayne **14** (85%) as a deep orange powder.† At low cone voltage in the presence of a small amount of $AgNO_3$,[9] the electrospray (ES) MS of **14** contained peaks at high molecular masses, corresponding to the dimeric Ag^+-bridged species $[\{W_2(\mu\text{-}C_8)(CO)_6(\eta\text{-}C_5H_5)_2\}_2(\mu\text{-}Ag)]^+$ (*m*/*z* 1631) and the $[Ag(NCMe)]^+$-coordinated species $[\{W_2(\mu\text{-}C_8)(CO)_6(\eta\text{-}C_5H_5)_2\}Ag(NCMe)]^+$ (*m*/*z* 911). At higher cone voltages, fragmentation due to the successive loss of CO ligands from **14** was observed.

The reactivity of the triple bonds in some of these compounds has also been probed. Reactions between $[Co_2(CO)_8]$ and **1** or **8** occurred at the less sterically hindered C≡C triple bonds to yield the derivatives $[Co_2\{\mu\text{-}RC_2C{\equiv}C[W(CO)_3(\eta\text{-}C_5H_5)]\}(CO)_6]$ [R = H **15**, $Fe(CO)_2(\eta\text{-}C_5H_5)$, respectively]. We have recently described the related compounds $[Co_2\{\mu\text{-}RC_2C{\equiv}C[W(CO)_3(\eta\text{-}C_5H_5)]\}(\mu\text{-}dppm)(CO)_4]$ (R = H, $SiMe_3$).[10] However, treatment of **5**, **6** or **7**, in which both ends of the diynyl chain are terminated by bulky $M(CO)_3(\eta\text{-}C_5H_5)$ groups (M = Mo, W), with $[Co_2(CO)_8]$ is a novel route to the $MCo_2(\mu_3\text{-}C)$ cluster-capped acetylenes $[\{Co_2M(\mu_3\text{-}C)(CO)_8(\eta\text{-}C_5H_5)\}(\mu\text{-}C{\equiv}C)\{Co_2M'(\mu_3\text{-}C)(CO)_8(\eta\text{-}C_5H_5)\}]$ (M = M' = Mo **16a**, W **16b**; M = Mo, M' = W **16c**) in 20–40% yield. Their crystallographically determined structures are similar to that reported for $[\{Co_3(\mu_3\text{-}C)(CO)_9\}_2(\mu\text{-}C{\equiv}C)]$[11] and will be described elsewhere; the bridging C_4 ligand originally present in **1** has been formally oxidised to a dicarbyne.[1c]

Facile oxidative addition reactions of **1** with $[Ru_3(CO)_{10}L_2]$ (L = NCMe, L_2 = dppm) give hydrido clusters containing $\mu_3\text{-}\eta^1,\eta^2$-bonded alkynyl ligands in high yield. Thus, the reaction between $[Ru_3(\mu\text{-}dppm)(CO)_{10}]$ and 1.5 equiv. of **1** afforded $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1,\eta^2\text{-}C_2C{\equiv}C[W(CO)_3(\eta\text{-}C_5H_5)]\}(\mu\text{-}dppm)(CO)_7]$ **17**† (92%), which has been fully characterised crystallographically. In solution at room temp. this complex exists as an interconvertible mixture of isomers (*ca.* 2:1), the major component showing the usual windscreen-wiper motion found for cluster-bound acetylide ligands.[12] The minor isomer contains the μ-diynyl ligand locked between the phenyl rings of the μ-dppm ligand in a manner similar to that found in $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1,\eta^2\text{-}C_2C{\equiv}CSiMe_3)(\mu\text{-}dppm)_2(CO)_5]$.[10]

In conclusion, simple procedures have been developed which make **1** a readily available precursor for the synthesis of a range of new diyndiyl complexes. Other examples of the rich chemistry afforded by **1**, and related complexes such as **4** and **11**, will be the subject of future reports.

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Footnote

† All new complexes have satisfactory C, H analyses. *Selected spectroscopic data*: **1** IR (CH_2Cl_2): ν(C≡C) 2145m; ν(CO) 2044s, 1958s (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.66 (5 H, s, C_5H_5), 2.03 (1 H, s, C≡CH). ^{13}C NMR ($CDCl_3$): δ 227.41 (t, J_{CW} 70 Hz, CO), 210.87 (t, J_{CW} 70 Hz, CO), 110.52 (br, C_α), 91.51 (s, C_5H_5), 71.60 (t, J_{CW} 44 Hz, C_β), 70.13 (t, J_{CW} 47 Hz, C_γ), 63.30 (s, C_δ). ESMS: (low cone voltage) *m*/*z* 396, $[M + MeCN + H - CO]^+$; 368, $[M + NCMe + H - 2CO]^+$; 355, $[M + H - CO]^+$; (high cone voltage) *m*/*z* 299, $[M + H - 3CO]^+$. **5** IR (CH_2Cl_2): ν(C≡C) 2145w; ν(CO) 2043s, 2037s, 1955s (br) cm^{-1}. ESMS: (low cone voltage) *m*/*z* 687, $[M + H - CO]^+$; (high cone voltage) *m*/*z* 687–547, $[M + H - nCO]^+$ (*n* = 1–6). **13** IR (CH_2Cl_2): ν(C≡C) 2183m, 2059m; ν(CO) 2038vs, 1956s (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.27–7.46 (5 H, m, Ph), 5.68 (5 H, s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 227.60 (t, J_{CW} 60 Hz, CO), 210.64 (t, J_{CW} 71 Hz, CO), 132.38 (s, *o*-C), 128.16 (s, *m*-C), 127.97 (s, *p*-C), 123.05 (s, *ipso*-C), 111.03 (t, J_{CW} 11 Hz, C_α), 91.62 (s, C_5H_5), 76.19, 73.78 (2 × s, C_γ and C_δ); C_β not observed. FABMS: *m*/*z* 458, M^+; 430, $[M - CO]^+$. **14** IR (CH_2Cl_2): ν(C≡C) 2190w; ν(CO) 2043s, 1959vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.67 (s, 5 H, C_5H_5), 5.32 (s, < 1 H, CH_2Cl_2). ^{13}C NMR ($CDCl_3$): δ 227.32 (s, CO), 210.26 (s, CO), 112.39 (br, C_α), 91.66 (s, C_5H_5), 91.60 (s, C_β), 63.70 (s, C_γ), 60.91 (s, C_δ). **17** IR (CH_2Cl_2): ν(CO) 2062m, 2054m, 2037s, 2004vs, 1981s, 1948vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.63–7.10 (m, 60 H, Ph), 5.65 [s, 10 H, C_5H_5(1)], 5.50 [s, 5 H, C_5H_5(2)], 4.39, 3.53 [2 × dt, J_{HH} 13, J_{HP} 11 Hz, 2 × 2 H, CH_2P_2(1)], 4.39, 3.17 [2 × dt, J_{HH} 12, J_{HP} 12 Hz, 2 × 1 H, CH_2P_2(2)], −19.21 [m, 2 H, μ-H(1)], −19.74 [t, J_{HP} 15 Hz, 1 H, μ-H(2)]. ESMS: *m*/*z* (high cone voltage with NaOMe added) 1289, $[M + Na]^+$; 1261, $[M + Na - CO]^+$; (negative ion, with NaOMe added) 1297, $[M + OMe]^-$; 1265, $[M - H]^-$.

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