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 C₄ 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 divnyl 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 $[W(C \equiv CC \equiv CR)(CO)_3(\eta - C_5H_5)] (R = SiMe_3, Ph, PPh_2); (iv)$ new heterometallic clusters containing $\mu_3, \eta^1: \mu_3, \eta^1-CC \equiv CC$ 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 NHEt₂ solution of [WCl(CO)₃(η -C₅H₅)] 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 $[W(C\equiv CC\equiv CH)(CO)_3(\eta-C_5H_5)]$ 1 (Scheme 1) was isolated as a bright yellow powder (90%) after column chromatography on Al_2O_3 .† Similar reactions with, for example, $[MoCl(CO)_3(\eta-C_5H_5)]$, $[FeCl(CO)_2(\eta-C_5H_5)]$ and $[PtCl_2(dppe)]$, gave $[Mo(C\equiv CC\equiv CH)(CO)_3(\eta-C_5H_5)]$ 2 (60%), $[Fe(C\equiv CC\equiv CH)-(CO)_2(\eta-C_5H_5)]$ 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 v(C=C) absorption near 2150 cm⁻¹, while in their ¹³C 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 ¹⁸³W (*J*_{CW} typically 60–70 Hz). The C_{β} and C_{γ} carbons of 1 also displayed longer-range coupling to ¹⁸³W, 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(η -C₅H₅)] to a solution of 1 in thf–NHEt₂ containing a catalytic amount of CuI resulted in the formation of the bismetallated diynediyl complex [{(η -C₅H₅)(CO)₃W}₂(μ -C=CC=C)] **5** (80%) as a rather insoluble yellow powder.[†] The Mo analogue **6** (77%) and the heterobimetallic complexes {(η -C₅H₅)(CO)₃W}C=CC=C{Mo(CO)₃(η -C₅H₅)}] **7** (95%), [{(η -C₅H₅)(CO)₃W}C=CC=C{Fe(CO)₂(η -C₅H₅)}] **8** (65%)^{3b} and [Pt{C=CC=C[W(CO)₃(η -C₅H₅)]}₂(dppe)] **9** (74%) were prepared using the same methodology with the appropriate chloro– metal precursors.

Whilst attempts to react 1 with BuⁿLi 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, NHEt₂, $[ML_n]Cl$; ii, CuI, NHEt₂, $[PtCl_2(dppe)]$; iii, LDA, SiClMe₃; iv, C₆H₅I, $[Pd(PPh_3)_4]$, CuI; v, [Cu(tmeda)]Cl, O₂; vi, $[Co_2(CO)_8]$. Yields in parentheses.

with SiClMe₃, PClPh₂ or [MnBr(CO)₅] to give [W(C=CC=CSi- $Me_3)(CO)_3(\eta-C_5H_5)$] 10 (80%), [W(C=CC=CPPh_2)(CO)_3(\eta-C_5H_5)] (25%)and $[{(\eta-C_5H_5)(CO)_3W}C\equiv CC\equiv$ $C_{5}H_{5}$ 11 C{Mn(CO)₅}] 12 (20%), respectively.

The terminal divnyl ligand can be coupled with iodoarenes in the presence of catalytic amounts of [Pd(PPh₃)₄] and CuI. Thus $[W(C=CC=CPh)(CO)_3(\eta-C_5H_5)]$ 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(PPh₃)(NO)(η^{5} - C_5Me_5 $\}_2(\mu-C_8)$ and $[{Fe(dppe)(\eta^5-C_5Me_5)}_2(\mu-C_8)]^7$ have been prepared by oxidative coupling of the appropriate diynyl complexes using Cu(O₂CMe)₂ in pyridine at elevated temperatures. Similar attempts to prepare $[{(\eta-C_5H_5)(CO)_3W}_2(\mu C_8$] 14 resulted only in extensive decomposition of 1. However, under the milder Hay conditions (Cu₂Cl₂-tmeda, O₂ 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 AgNO₃,9 the electrospray (ES) MS of 14 contained peaks at high molecular masses, corresponding to the dimeric Ag⁺-bridged species [{ $W_2(\mu-C_8)(CO)_6(\eta-C_5H_5)_2$ }₂(μ -Ag)]⁺ (m/z 1631) and the [Ag(NCMe)]⁺-coordinated species $[{W_2(\mu-C_8)(CO)_6(\eta-C_5H_5)_2}Ag(NCMe)]^+ (m/2 911).$ 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 $[Co_2\{\mu-RC_2C\equiv C[W(CO)_3(\eta-C_5H_5)]\}(CO)_6]$ $[R = H 15, Fe(CO)_2(\eta - C_5H_5), respectively]$. We have recently described the related compounds $[Co_2\{\mu - RC_2C \equiv C[W(CO)_3(\eta - C_5H_5), respectively]]$ C_5H_5]}(μ -dppm)(CO)₄] (R = H, SiMe₃).¹⁰ However, treatment of 5, 6 or 7, in which both ends of the diynyl chain are terminated by bulky $M(CO)_3(\eta-C_5H_5)$ groups (M = Mo, W), with $[Co_2(CO)_8]$ is a novel route to the $MCo_2(\mu_3-C)$ clustercapped acetylenes $[{Co_2M(\mu_3-C)(CO)_8(\eta-C_5H_5)}(\mu-C\equiv C)$ $\{Co_2M'(\mu_3-C)(CO)_8(\eta-C_5H_5)\}\}$ (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 μ_3 - η^1, η^2 -bonded alkynyl ligands in high yield. Thus, the reaction between $[Ru_3(\mu-dppm)(CO)_{10}]$ and 1.5 equiv. of 1 afforded $[Ru_{3}(\mu-H)\{\mu_{3}-\eta^{1},\eta^{2}-C_{2}C\equiv C[W(CO)_{3}(\eta-C_{5}\hat{H}_{5})]\}(\mu-dppm)-$

(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 [Ru₃(μ -H) $(\mu_3 - \eta^1, \eta^2 - C_2 C \equiv CSiMe_3)(\mu - dppm)_2(CO)_5]$.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 (CH₂Cl₂): v(C≡C) 2145m; v(CO) 2044s, 1958s (br) cm⁻¹. ¹H NMR (CDCl₃): δ 5.66 (5 H, s, C₅H₅), 2.03 (1 H, s, C=CH). ¹³C NMR (CDCl₃): δ 227.41 (t, J_{CW} 70 Hz, CO), 210.87 (t, J_{CW} 70 Hz, CO), 110.52 $(br, C_{\alpha}), 91.51 (s, C_5H_5), 71.60 (t, J_{CW} 44 Hz, C_{\beta}), 70.13 (t, J_{CW} 47 Hz, C_{\gamma}),$ 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 (CH₂Cl₂): v(C=C) 2145w; v(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 (CH₂Cl₂): v(C=C) 2183m, 2059m; v(CO) 2038vs, 1956s (br) cm⁻¹. ¹H NMR (CDCl₃): § 7.27-7.46 (5 H, m, Ph), 5.68 (5 H, s, C₅H₅). ¹³C NMR (CDCl₃): 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 If Π_{c} , C_{o} , Γ_{o} , 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, C₈). 17 IR (CH₂Cl₂): v(CO) 2062m, 2054m, 2037s, 2004vs, 1981s, 1948vs cm⁻¹. ¹H NMR (CDCl₃): δ 7.63–7.10 (m, 60 H, Ph), 5.65 [s, 10 H, $C_{5}H_{5}(1)$], 5.50 [s, 5 H, $C_{5}H_{5}(2)$], 4.39, 3.53 [2 × dt, J_{HH} 13, J_{HP} 11 Hz, 2 \times 2 H, CH₂P₂(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][–].

References

- 1 (a) C. J. Adams, M. I. Bruce, E. Horn, B. W. Skelton, E. R. T. Tiekink and A. H. White, J. Chem. Soc., Dalton Trans., 1993, 3299; 3313; (b) M. I. Bruce, P. Hinterding, E. R. T. Tiekink, B. W. Skelton and A. H. White, J. Organomet. Chem., 1993, 450, 209; (c) M. I. Bruce, L. I. Denisovich, P. J. Low, S. M. Peregudova and N. A. Ustynyuk, Mendeleev Commun., 1996, 200.
- W. Beck, B. Niemer and M. Wieser, Angew. Chem., Int. Ed. Engl., 1993, 32, 923; H. Lang, Angew. Chem., Int. Ed. Engl., 1994, 33, 547.
- 3 (a) K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Hagihara, J. Organomet. Chem., 1978, 145, 101; (b) A. Wong, P. C. W. Kang, C. D. Tagge and D. R. Leon, Organometallics, 1990, 9, 1992; (c) H. B. Fyfe, M. Mlekuz, D. Zagarina, N. J. Taylor and T. B. Marder, J. Chem. Soc., Chem. Commun., 1991, 188; (d) Y. Sun, N. J. Taylor and A. J. Carty, Organometallics, 1992, 11, 4293; (e) R. Crescenzi and C. Lo Sterzo, Organometallics, 1992, 11, 4301; (f) H. Werner, O. Gevert, P. Steinert and J. Wolf, Organometallics, 1995, 14, 1786; (g) N. Le Narvor, L. Toupet and C. Lapinte, J. Am. Chem. Soc., 1995, 117, 7129; (h) W. Weng, T. Bartik, M. Brady, B. Bartik, J. A. Ramsden, A. M. Arif and J. A. Gladysz, J. Am. Chem. Soc., 1995, 117, 11922.
- 4 K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Hagihara, J. Organomet. Chem., 1978, 145, 101; M. V. Russo and A. Furlani, J. Organomet. Chem., 1979, 165, 101; M. I. Bruce, M. G. Humphrey, J. G. Matisons, S. K. Roy and A. G. Swincer, Aust. J. Chem., 1984, **37**, 1955.
- 5 L. Brandsma, Preparative Acetylenic Chemistry, Elsevier, Amsterdam, 1988, p. 178
- 6 M. Brady, W. Weng and J. A. Gladysz, J. Chem. Soc., Chem. Commun., 1994, 2655.
- 7 F. Coat and C. Lapinte, Organometallics, 1996, **15**, 477. 8 A. S. Hay, J. Org. Chem., 1962, **27**, 3320.
- 9 B. K. Nicholson and W. Henderson, J. Chem. Soc., Chem. Commun., 1995. 2531.
- 10 M. I. Bruce, P. J. Low, A. Werth, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans., 1996, 1551.
- 11 R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson and J. L. Spencer, Inorg. Chem., 1970, 9, 2204.
- 12 G. Predieri, A. Tiripicchio, C. Vignali and E. Sappa, J. Organomet. Chem., 1988, 342, C33.

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