New forms of coordinated carbon: Wirelike cumulenic C_3 and C_5 sp carbon chain that span two different transition metals and mediate charge transfer.

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Reactions of (η^5-C_5Me_5)Re(NO)(PPh_3)(C ⋮ CLi) with $W(CO)_6$, $Fe(CO)_5$, or $Mn(CO)_3(\eta^5$-$C_5H_nCl_{5-n})$, followed by Me_3O^+ BF_4^-, give the heterobimetallic C_3OMe complexes (η^5-C_5Me_5)Re(NO)(PPh_3)(C ⋮ CC(OMe))$M(CO)_x(\eta^5$-$C_5H_nCl_{5-n})_y$ (M/*x*/*y*/*n* = **3**, W/5/0/−; **4**, Fe/4/0/−; **5**, Mn/2/1/5; **6**, Mn/2/1/4; **7**, Mn/2/1/0). Spectroscopic and crystallographic (**3**) data indicate contributions by $^+$ReCCC(OMe)−M^- resonance forms. Reactions of **4**−**7** and BF_3 gas give the title compounds [(η^5-C_5Me_5)Re(NO)(PPh_3)(CCC)$M(CO)_x(\eta^5$-$C_5H_nCl_{5-n})_y$ (M/*x*/*y*/*n* = **9**, Mn/2/1/5; **10**, Mn/2/1/4; **11**, Mn/2/1/0; **12**, Fe/4/0/−). Spectroscopic and crystallographic (**9**) data indicate dominant contributions by fully cumulated $^+$ReCCCMn resonance forms. Reactions of (η^5-C_5Me_5)Re(NO)(PPh_3)(C ⋮ CC ⋮ CLi) with $Mn(CO)_3(\eta^5$-$C_5Cl_5)$, $Mn(CO)_3(\eta^5$-$C_5Br_5)$, or $Fe(CO)_5$, followed by Me_3O^+ BF_4^-, give the C_5OMe complexes (η^5-C_5Me_5)Re(NO)(PPh_3)(C ⋮ CC ⋮ CC(OMe))$M(CO)_x(\eta^5$-$C_5X_5)_y$ (M/*x*/*y*/X = **16**, Mn/2/1/Cl; **19**, Mn/2/1/Br; **20**, Fe/4/0/−). However, $Mn(CO)_3(\eta^5$-$C_5H_5)$ does not react. Reaction of **16** and BF_3 gives the C_5 complex [(η^5-C_5Me_5)Re(NO)(PPh_3)(CCCCC)$Mn(CO)_2(\eta^5$-$C_5Cl_5)]^+$ BF_4^- (**21**) as a light-sensitive deep brown powder of >94% purity. IR and NMR data show a dominant $^+$ReCCCCCMn resonance form. UV−visible spectra of **9**−**11** and **21** show intense absorptions at 392, 396, 414, and 480 nm (ε 55 800, 50 900, 49 100, 60 500 M^{-1} cm^{-1}), respectively, and weaker longer wavelength bands. These are believed to have appreciable rhenium-to-manganese charge-transfer character.

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https://www.acs.org/content/acs/en.html