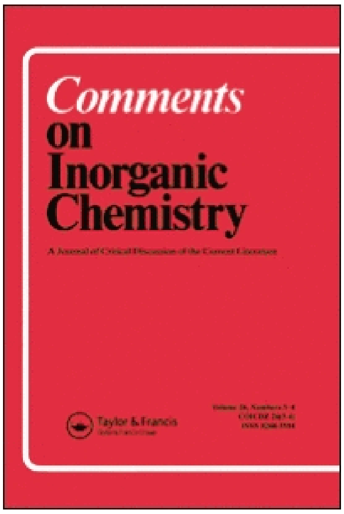

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THE ODD BIT OF CARBON

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Anthony Hill joined Gordon Stone's research group as a postdoctoral research assistant from 1986-8 in the halcyon days of the "E317" lab at the University of Bristol. The supportive environment of creative and imaginative synthetic design that Gordon fostered in Bristol was unparalleled, quite without apology for the pursuit of curiosity-driven science that bordered on molecular fine arts. In 1996 Gordon handed over the reins of *Advances in Organometallic Chemistry*, the journal series, now running to some 60 volumes, which Gordon inaugurated in 1964 with Bob West. During Gordon's mid-career phase, when he had a mere 400 publications to his name, carbyne chemistry held special interest for him. The work to follow reflects the enthusiasm those times engendered in this intriguing class of compounds.

Keywords: alkylidyne, carbido, carbyne, metallacumulene, tricarbido

Abbreviations: Cp = η^5-C_5H_5, Cp′ = η^5-$C_5H_xCl_{5\text{-}x}$, Tp = hydrotris(pyrazolyl)borate, Tp* = hydrotris(dimethylpyrazolyl)borate, pz = pyrazol-1-yl, TBAF = [^{n}Bu$_4$N]F (1.0 M in THF)

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METALS LINKED BY AN ODD NUMBER OF CARBON ATOMS

Through the work of *inter alia*, Bruce, Gladysz, Dixneuf, Templeton, Akita and Lapinte, the study of bimetallic compounds in which two metal centers are spanned by a single linear chain of carbon atoms, "dimetallapolycarbyls" has matured enormously.[1] The rapid advances in this field owe much to the existence of robust methodologies for the manipulation of organic alkynes and poly-ynes that could be readily adapted to afford organometallic analogues. A corollary of this reliance on alkyne chemistry, which effectively delivers carbon in units of two ("C≡C"), was that by the outset of our studies the overwhelming majority of examples were based on bimetallics bridged by even-numbered carbon chains with localised poly-yn-diyl bonding manifolds (Figure 1).

A small number of monocarbido[2] and tricarbido[3] bimetallics had been reported in addition to one somewhat unstable pentacarbido example.[3c] This situation presented a challenge for the further development of "dimetallapolycarbyl" chemistry in that one driving force had previously been the possibility of electronic communication between metal centers. Such communication should certainly be enhanced by the presence of metal-carbon multiple bonding that simple electronic bookkeeping indicates is essential for odd-numbered carbon chains. We therefore set about attempting to prepare bimetallic complexes

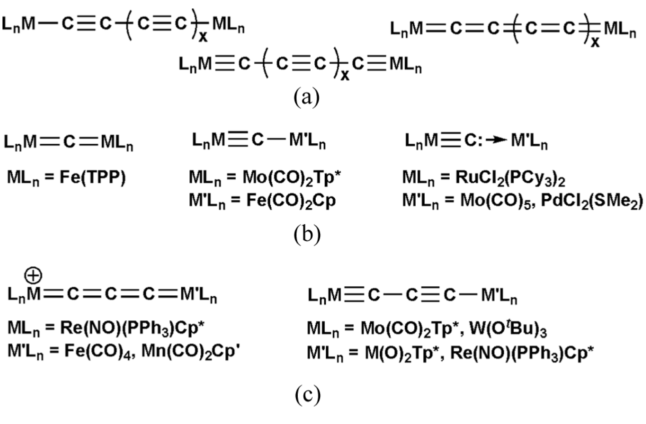


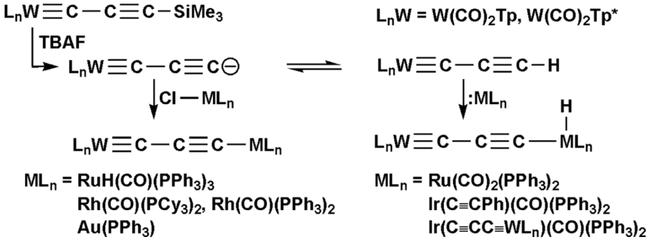
Figure 1. (a) Poly-yn-diyl, cumulenic and poly-yn-diylidyne (bis-carbyne) descriptions of dimetallapolycarbyls. (b) Selected bimetallic monocarbido complexes. (c) Selected bimetallic tricarbido complexes.

spanned by odd numbered carbon chains via routes that might promise a degree of general applicability.

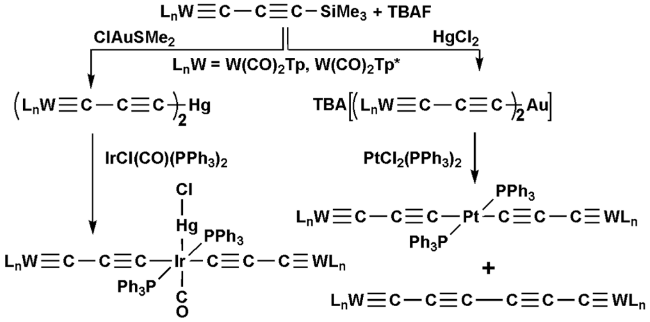
TRICARBIDO COMPLEXES

Given that expedient routes to propargylidynes [$L_nM{\equiv}C\text{-}C{\equiv}C\text{-}R$] had been previously developed by Stone,[4] these reagents appeared to be ideal pre-fabricated "C_3" building block. In particular, the possibility of fluoride-mediated protodesilylation of silyl propargylidynes [$L_nM{\equiv}C\text{-}C{\equiv}C\text{-}SiMe_3$][4b] appeared to offer the possibility of generating either parent propargylidyne species [$L_nM{\equiv}C\text{-}C{\equiv}C\text{-}H$] or their conjugate bases [$L_nM{\equiv}C\text{-}C{\equiv}C$]$^-$ (Scheme 1). In practice, both species are generated when moist TBAF is used to desilylate a variety of silylpropargylidyne complexes. Whilst neither species could be isolated, they could be trapped by suitable transition metal complexes.[5–8] When suitable metal halide complexes were employed, simple halide metathesis occurred. However, when electron-rich complexes devoid of labile halide ligands were employed, e.g., [$Ru(CO)_2(PPh_3)_3$] or [$Ir(C{\equiv}CPh)(CO)(PPh_3)_2$], C–H activation occurred to afford hydrido-tricarbido complexes. In the case of Vaska's complex, [$IrCl(CO)(PPh_3)_2$], both processes occurred to afford bis(tricarbido)iridum species [$IrH(C{\equiv}C\text{-}C{\equiv}W(CO)_2L)_2(CO)(PPh_3)_2$] ($L = Tp, Tp^*$).[6]

The uncertainty as to whether the silypropargylidyne/TBAF combination would perform as [$L_nM{\equiv}C\text{-}C{\equiv}C\text{-}H$] or [$L_nM{\equiv}C\text{-}C{\equiv}C$]$^-$ could be overcome by the synthesis of crystalline gold[7] or mercury[8] tricarbido derivatives, which serve as tricarbido transmetallating agents towards rhodium,[9] ruthenium,[10] iridium[11] and platinum complexes (Scheme 2).[12]



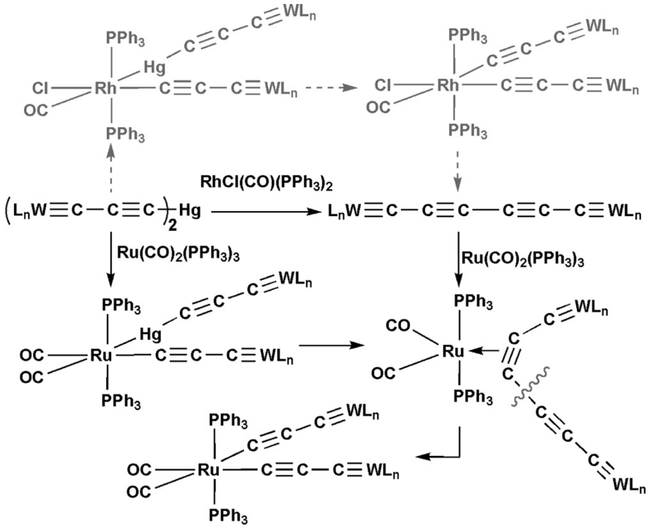
Scheme 1. Synthesis of bimetallic tricarbido complexes via fluoride mediated protodesilylation of propargylidynes (selected examples).



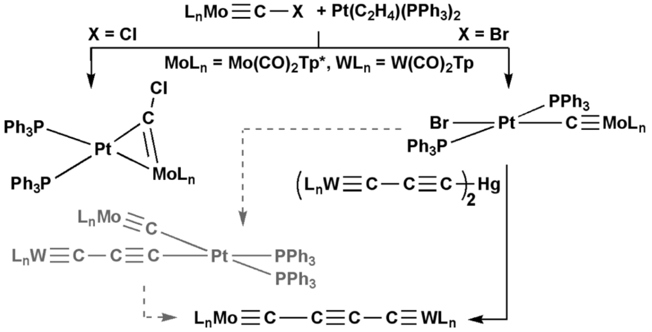
Scheme 2. Synthesis of gold and mercury tricarbido transmetallating agents.

DIMETALLAOCTATETRAYNES AND DIMETALLAHEXATRIYNES

Whilst exploring transmetallation reactions with the tricarbido mercurials, we encountered an unusual reaction in which Vaska's complex afforded a bis(tricarbido)iridium(III) species, which included a chloromercurio ligand (Scheme 3).[11] The corresponding reaction with the rhodium analogue however took a different course: [RhCl(CO)(PPh$_3$)$_2$] is known to catalytically demercurate bis(alkynyl)mercurials providing



Scheme 3. Catalytic demercuration of bis(tricarbido) mercurials.



Scheme 4. Synthesis of a dimetallahexatriyne.

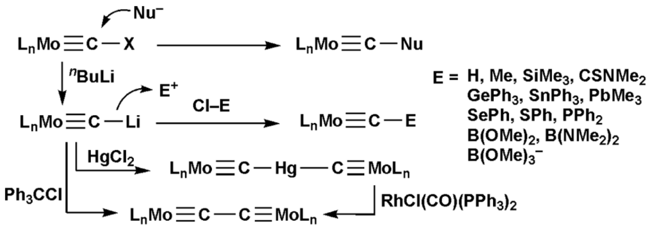
1,3-diynes[13] and a similar sequence operates with bis(tricarbido)mercurials to afford the first examples of dimetallaoctatetraynes (Scheme 3).[9]

The cis-reductive elimination of two tricarbido units from rhodium is mechanistically implicit in the formation of these species and it is therefore remarkable to note that the reactions of these octatetraynes with $[Ru(CO)_2(PPh_3)_3]$ results in insertion of the ruthenium center into the central single bond of the poly-yne spine.[10]

The synthesis of dimetallaoctateraynes via $[3+3]$ reductive elimination suggested a potential route to dimetallahexatriynes via a $[3+1]$ reductive coupling strategy. The reaction of Lalor's halocarbyne complexes $[Mo(\equiv CX)(CO)_2Tp^*]$ ($X = Cl$, Br)[14] with $[Pt(C_2H_4)(PPh_3)_2]$ affords either the bridging carbyne complex $[MoPt(\mu\text{-}CCl)(CO)_2(PPh_3)_2Tp^*]$ or the bimetallic carbido complex $[MoPt(\mu\text{-}C)Br(CO)_2(PPh_3)_2Tp^*]$. The latter upon treatment with $Hg\{C_3W(CO)_2Tp^*\}_2$ affords the unsymmetric complex $[WMo(\mu\text{-}C_4)(CO)_4TpTp^*]$ (Scheme 4).[15]

CARBIDO COMPLEXES AND LITHIATED CARBYNES

The typical reactions of Lalor's halocarbyne complexes involve *nucleophilic* ("Nu^-") substitution of the halide substituent,[16] a process which may be catalyzed in some cases by palladium(0).[17] An alternative method for the C-functionalization of halocarbynes involves low temperature lithium-halogen exchange with ^nBuLi, an approach that effects a carbyne "umpolung" such that substituents may be introduced in *electrophilic* ("E^+") form (Scheme 5).[18] This affords convenient, "one pot" access to a wide range of main group element substituted carbyne

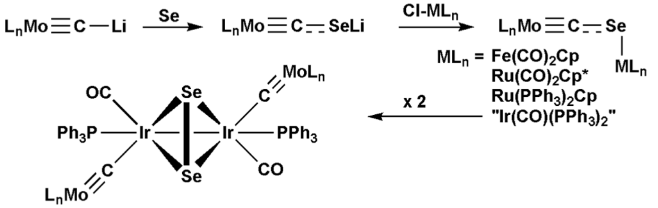


Scheme 5. Electrophilic installation of carbyne substituents via umpolung.

complexes from a single common intermediate, including examples based on boron, carbon, silicon, germanium, tin, lead, sulfur, selenium and tellurium.

Furthermore, transition metal electrophiles may be employed, thereby affording a direct route to bi and trimetallic carbido bridged complexes (Scheme 6). Amongst these, the mercury derivative $Hg\{C{\equiv}Mo(CO)_2Tp^*\}_2$ is noteworthy in that in keeping with the catalytic demercuration of bis(tricarbido)mercurials described above, treating this species with $[RhCl(CO)(PPh_3)_2]$ results in the mercury-free ethane-diylidyne complex thereby completing the bis(carbyne) series $[M_2(\mu\text{-}C_n)(CO)_4L_2]$ (n = 2,4,6; L = Tp, Tp*; M = Mo, W).

The reaction of the lithiated carbyne with elemental chalcogens affords a convenient route to the chalcocarbonyl metallates $[Mo(CE)(CO)_2Tp^*]^-$ (E = S, Se, Te).[18] In keeping with the reactions of alkynylselenolates with metal halides,[20] the anionic selenocarbonyl complex reacts with a variety of transition metal halides to afford isoselenocarbonyl bridged bimetallics. In the case of Vaska's complex, whilst an isoselenocarbonyl might be a plausible intermediate, this undergoes subsequent insertion of iridium into the C–Se bond to afford a novel bis(carbido) complex based on an Ir_2Se_2 tetrahedrane core (Scheme 6).



Scheme 6. Selenocarbony, isoselenocarbonyl and carbido complexes.

CONCLUSIONS

Synthetic routes have been developed allowing access to a wide range of bi- and polymetallic species, which are bridged by carbido or tricarbido units. A tangent to this program has involved the observation that halogen-lithium exchange processes operate for halocarbyne ligands, resulting in an umpolung of the conventional reactivity of these carbon centers and allowing the introduction of diverse carbyne substituents in electrophilic form, including further transition metals.

ACKNOWLEDGEMENTS

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