5576 *Organometallics* **2005,** *24,* 5576−5580

Neutral and Anionic Tricarbido Complexes of Gold(I)

Rian D. Dewhurst, Anthony F. Hill,* and Matthew K. Smith

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory, Australia

Received June 27, 2005

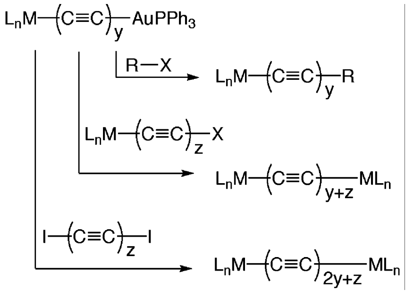
Desilylation of $[W(\equiv CC\equiv CSiMe_3)(CO)_2L]$ (L = $HB(pz)_3$, $HB(pz')_3$; pz = pyrazol-1-yl, pz′ = 3,5-dimethylpyrazol-1-yl) with $[Bu_4N]F$ in the presence of $[AuCl(PPh_3)]$ provides the neutral complexes $[W(\equiv CC\equiv CAuPPh_3)(CO)_2L]$ in addition to traces of the salt $[Bu_4N][Au(C\equiv CC\equiv W(CO)_2\{HB(pz)_3\})_2]$. The corresponding salt $[N(PPh_3)_2][Au(C\equiv CC\equiv W(CO)_2\{HB(pz')_3\})_2]$ may be obtained in high yield via the reaction of $[W(\equiv CC\equiv CSiMe_3)(CO)_2\{HB(pz')_3\}]$ with methanolic KOH in the presence of $[AuCl(SMe_2)]$.

Introduction

Within the rapidly growing field of mono- and dimetallapolycarbyl chemistry,[1] gold(I)-based examples L_nMC_xAuL' and $L'AuC_xAuL'$ attract particular interest due primarily to their optical properties,[2] but more recently as effective (poly)alkynyl transfer agents.[3] Cross has demonstrated stoichiometric alkynyl transfer processes from gold alkynyls of the form $[RC\equiv CAuPPh_3]$ to a range of platinum halide complexes and to mercury.[4] Such processes are implicit in the remarkably versatile synthetic protocols developed recently by Bruce for the palladium-mediated modular construction of long-chain dimetallapolycarbyls in which the precursors are gold(I)- and halide-terminated derivatives of the constituent modules (Scheme 1).

Dimetallapolycarbyls are by far most represented by compounds in which two metals are linearly spanned by an even number of carbon atoms, by virtue of well-established alkyne coupling protocols that may often be extended to metal-terminated derivatives.[1] We have recently addressed the paucity of general synthetic routes to odd-numbered carbon chain spacers by developing routes to tricarbido (C_3)-linked systems in which tungsten is linked to the metals Ru, Rh, Ir, Hg, and (transiently) Pt.[5] Prior to our work, tricarbido complexes were limited in number to the archetypes provided by Gladysz[6] and Templeton.[7] Herein we report the synthesis of the first examples of neutral and anionic gold tricarbido derivatives, which one might anticipate will serve as useful tricarbido transfer reagents.

Scheme 1. Carbon−Carbon Bond Forming Reactions of Aurometallapolycarbyls Mediated by $[Pd(PPh_3)_4]/CuI$[3]



Results and Discussion

The classical approach to the synthesis of gold(I) alkynyls involves the reaction of gold(I) halide complexes, e.g., $[AuCl(PPh_3)]$, with terminal alkynes in the presence of a base, most commonly sodium alkoxide.[4,10,11] The propargylidyne complexes $[W(\equiv CC\equiv CSiMe_3)(CO)_2L]$ (**1a**, **1b**; hereafter **a** indicates L = $HB(pz)_3$ and **b** denotes L = $HB(pz')_3$; pz = pyrazol-1-yl,

---

(1) (a) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179. (b) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2002**, *48*, 71.

(2) (a) Jia, G.; Puddephatt, R. J.; Vittal, J. J.; Payne, N. C. *Organometallics* **1993**, *12*, 263. (b) Jia, G.; Puddephatt, R. J.; Vittal, J. J.; Payne, N. C. *Organometallics* **1993**, *12*, 4771. (c) Jia, G.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics*, **1993**, *12*, 3565. (d) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541.

(3) (a) Bruce, M. I.; Humphrey, P. A.; Melino, G.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Inorg. Chim. Acta* **2005**, *358*, 1453. (b) Antonova, A. B.; Bruce, M. I.; Ellis, B. G.; Gaudio, M.; Humphrey, P. A.; Jevric, M.; Melino, G.; Nicholson, B. K.; Perkins, G. J.; Skelton, B. W.; Stapleton, B.; White, A. H.; Zaitseva, N. N. *Chem. Commun.* **2004**, 960. (c) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **2003**, *683*, 398. (d) Bruce, M. I.; Smith, M. E.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2003**, *670*, 170.

(4) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411.

(5) (a) Dewhurst, R. D.; Hill, A. F.; Smith, M. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 476. (b) Dewhurst, R. D.; Hill, A. F.; Willis, A. C. *Organometallics* **2004**, *23*, 1646. (c) Dewhurst, R. D.; Hill, A. F.; Willis, A. C. *Organometallics* **2004**, *23*, 5903. (d) Dewhurst, R. D.; Hill, A. F.; Willis, A. C. *Chem. Commun.* **2004**, 2826. (e) Dewhurst, R. D.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 3043.

(6) (a) Weng, J. A. Ramsden, Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824. (b) Bartik, T.; Weng, W.; Ramsden, J. A.; Szafert, S.; Falloon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 11071. (c) Deminski, R.; Szafert, S.; Haquette, P.; Lis, T.; Gladysz, J. A. *Organometallics* **1999**, *18*, 5438.

(7) Woodworth, B. E.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 7418.

(8) The complexes **1** are readily available via Fischer's modification of the procedures developed for the complexes $[M(\equiv CC\equiv CCMe_3)(CO)_2L]$ (M = Mo, W):[9] (a) Schwenzer, B.; Schleu, J.; Burzlaff, N.; Karl, C.; Fischer, H. *J. Organomet. Chem.* **2002**, *641*, 134. (b) Schwenzer, B.; Fischer, H. *J. Organomet. Chem.* **2003**, *667*, 16.

(9) Hart, I. J.; Hill, A. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2261.

(10) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163.

(11) Cross, R. J.; Davidson, M. F.; McLennan, A. J. *J. Organomet. Chem.* **1984**, *265*, C37.

10.1021/om050528i CCC: $30.25

pz′ = dimethylpyrazol-1-yl)[8] are readily desilylated by $[Bu_4N]F$.[5a] Because of the water present in commercial $[Bu_4N]F$, it may be assumed that both the "parent" propargylidynes $[W(\equiv CC\equiv CH)(CO)_2L]$ and their conjugate bases are present. Indeed, reactions have been observed that implicate the intermediacy of both species.[5b] Accordingly, we anticipated that the reaction of **1** with $[AuCl(PPh_3)]$ and $[Bu_4N]F$ would provide the desired heterobimetallic tricarbido complexes $[W(\equiv CC\equiv CAuPPh_3)(CO)_2L]$ (**2a**, **2b**) directly, obviating the need to employ the parent propargylidynes that have to date eluded isolation. When a slight excess of **1a** is treated with $[NBu_4]F$ in the presence of $[AuCl(PPh_3)]$, no appreciable color change is noted; however a red compound was precipitated by addition of ethanol and slow concentration. This solid was found to be pure by spectroscopic techniques and was formulated as the tungsten−gold complex $[W(\equiv CC\equiv CAuPPh_3)(CO)_2\{HB(pz)_3\}]$ (**2a**). Attempts to obtain a second crop of **2a** from the filtrate yielded an impure orange solid, which contained only a trace of phosphine ligand ($^{31}P\{^1H\}$ NMR) and an approximate 2:1 ratio of $HB(pz)_3$:$[NBu_4]^+$ (^1H NMR, vide infra).

The solution infrared spectrum of **2a** showed a modest lowering of the stretching frequencies of the WCO associated bands (CH_2Cl_2: 1975, 1887 cm^{-1}, cf. 1991, 1906 cm^{-1} for **1a**) compared to the precursor, while that assigned to the $C\equiv C$ stretch was decreased by more than 40 cm^{-1} (2012 cm^{-1} **2a**, cf. 2056 cm^{-1} **1a**). The ^1H NMR spectrum showed the expected absence of $SiCH_3$ signals but only negligible shifts in the positions of the pyrazolyl proton resonances from those of the precursor. The $^{31}P\{^1H\}$ NMR spectrum displayed a singlet at δ_P 42.3, comparable to data previously reported for simple alkynyl complexes $[Au(C\equiv CR)(PPh_3)]$ (δ_P 41.1−42.3).[4] The $^{13}C\{^1H\}$ NMR spectrum of **2a** included low-field signals for the tricarbido C_α (δ_C 255.8) and WCO (δ_C 226.4) nuclei very close to those of **1a** with the $^{183}W-^{13}C$ coupling observed for both signals (196 and 168 Hz, respectively) being almost identical to those of **1a** (200, 164 Hz). As **2a** is the first example of a tricarbido complex in which the C_3 ligand is bound *trans* to a phosphine, the possibility arises of using the magnitude of $^nJ_{PC}$ couplings to infer the value of n. Interestingly, signals for the tricarbido C_β and C_γ nuclei were found at δ 121.3 and 126.8, respectively, their relative positions reversed from those of the precursor and other heterobimetallic tricarbido complexes.[5−7] Thus for **2a** the C_γ signal is shifted downfield somewhat and appears as a broad doublet ($^2J_{PC}$ = 129 Hz). The signal for C_β is in a position similar to that of **1a**, but appears as a broad doublet with $^3J_{PC}$ not being resolvable. The electrospray mass spectrum of **2a** in acetonitrile showed extensive fragmentation of the molecular ion and an abundant signal at *m/z* 1407 corresponding to the addition of a $[Au(PPh_3)]$ fragment to provide $[\mathbf{2a}\cdot AuPPh_3]^+$. It is not clear whether this fragmentation is a result of the spectroscopic conditions or scrambling of the molecule due to the presence of acetonitrile.

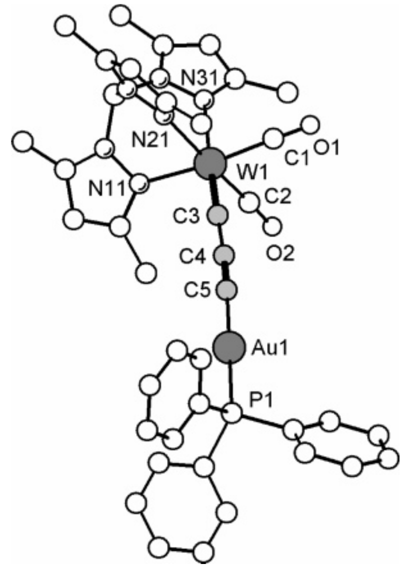


Figure 1. Molecular geometry of **2b** in a crystal (hydrogen atoms omitted; C3, C4, and C5 correspond respectively to C_α, C_β, and C_γ). Selected bond distances (Å) and angles (deg): Au1−C5 1.992(6), Au1−P1 2.2693(16), W1−C3 1.834(6), W1−C2 1.984(6), W1−C1 1.997(6), W1−N21 2.203(4), W1−N11 2.206(4), W1−N31 2.304(4), C3−C4 1.385(7), C4−C5 1.209(7), C5−Au1−P1 179.19(17), C3−W1−C2 85.8(2), C3−W1−C1 87.2(2), C2−W1−C1 86.6(2), C3−W1−N21 100.80(19), C1−W1−N21 95.87(19), C3−W1−N11 98.43(19), C2−W1−N11 95.18(19), N21−W1−N11 81.69(16), C2−W1−N31 91.78(19), C1−W1−N31 91.75(19), N21−W1−N31 81.62(15), N11−W1−N31 82.68(15), C4−C3−W1 177.4(4), C5−C4−C3 176.4(6), C4−C5−Au1 178.6(5).

The synthesis of $[W(\equiv CC\equiv CAuPPh_3)(CO)_2\{HB(pz')_3\}]$ (**2b**) from **1b** was achieved in a manner analogous to **2a**, a pure red solid being obtained in 72% yield by crystallization from CH_2Cl_2/ethanol. Spectroscopic data for **2b** are in all respects comparable to those of **2a** and call for no further comment. However, in the case of **2b**, crystallographic grade crystals were obtained, allowing a structure determination, the results of which are summarized in Figure 1. There exists a plethora of structural data for linear two-coordinate gold triarylphosphine alkynyls;[12] however the compounds $[Au(C\equiv CR)(PPh_3)]$ (R = Ph,[13] $SiMe_3$,[14] CMe_3,[14] $AuPPh_3$,[15] and $C\equiv CRu(PPh_3)_2(\eta\text{-}C_5H_5)$[16]) suffice for illustrative purposes. These representative complexes have Au−C separations in the narrow range 1.97−2.00 Å and $C\equiv C$ bond lengths of 1.180−1.196 Å. The complex $Ph_3PAuC\equiv CC\equiv CRu(PPh_3)_2(\eta\text{-}C_5H_5)$[16] provides a useful benchmark by illustrating the comparative effect of the closed shell d^{10}-Au^I substituent vs the strongly retrodative π-basic d^6-Ru^{II} terminus, reflected in the alkynyl group bound to ruthenium having $C\equiv C$ = 1.216 Å. For **2b**, the Au1−C5 distance of 1.992(6) Å is unremarkable and falls within the established range. The C4−C5 distance of 1.209(7) Å is somewhat elongated with respect to the above examples, but not significantly so. Similarly, there are many structural data for alkylidyne complexes of the "$W(CO)_2\{HB(pz')_3\}$" fragment[12] including tricarbido

---

[12] Cambridge Crystallographic Data Centre, Conquest Release, February 2005.

[13] Bruce, M. I.; Duffy, D. N. *Aust. J. Chem.* **1986**, *39*, 1697.

[14] Vincente, J.; Chieste, M.-T.; Abrisqueta, M.-D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

[15] Bruce, M. I.; Grundy, K. R.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *344*, C49.

[16] Bruce, M. I.; Ellis, B. G.; Gaudio, M.; Lapinte, C.; Melino, G.; Paul, F.; Skelton, B. W.; Smith, M. E.; Toupet, L.; White, A. H. *Dalton Trans.* **2004**, 1601.

examples,[5,17] and the W1−C3 separation of 1.834(6) Å falls within norms for W−C triple bonding.[18] These data taken together point toward a conventional localized W≡C−C≡C−Au valence bond description. The alkylidyne ligand exerts the characteristic *trans* influence associated with M−C multiple bonding such that the pyrazolyl group *trans* to the alkylidyne is significantly (25σ) displaced (W1−N31 = 2.304(4) Å) relative to those *trans* to the carbonyl ligands (W1−N21 2.203(4) Å, W1−N11 2.206(4) Å). The PPh_3 and $HB(pz')_3$ are sufficiently remote from each other that there are no intramolecular steric interactions of note. Similarly, examination of the crystal packing does not reveal any intermolecular Au···Au or C−H···π interactions; that is, the geometric parameters along the essentially linear N11−W1−C3−C4−C5−Au1−P1 spine reflect electronic factors alone.

It was noted that a phosphine-free side product was observed but not fully identified in the preparation of **1a**. We suspected this to be the salt $[Bu_4N][Au(C{\equiv}CC{\equiv}W(CO)_2\{HB(pz)_3\})_2]$, $[Bu_4N]$[**3a**], given that (i) we have recently isolated the isoelectronic mercurial $[Hg(C{\equiv}CC{\equiv}W(CO)_2\{HB(pz)_3\})_2]$[5d] and (ii) bis(alkynyl)aurates have long since been shown to arise from the reactions of $\{AuC{\equiv}CPh\}_n$ with KC≡CPh.[19] We have not succeeded in isolating $[Bu_4N]$[**3a**] in pure form; however it has been possible to develop a selective synthetic route to the corresponding $HB(pz')_3$ derivative, which may be isolated as either $[Bu_4N]^+$ or $[N(PPh_3)_2]^+$ salts; the former, $[Bu_4N]$[**3b**], provided crystals suitable for a crystallographic analysis, while the latter, $[N(PPh_3)_2]$[**3b**], was isolated in better yields. Thus the reaction of **1b**, $[Bu_4N]F$, and the labile gold complex $[AuCl(SMe_2)]$ resulted in essentially quantitative formation of $[Bu_4N]$[**3b**], although recovery in pure form from solution proved problematic. Replacing $[Bu_4N]F$ with methanolic KOH as the desilylating agent resulted in clean conversion to K[**3b**], which could easily be converted to $[N(PPh_3)_2]$[**3b**] by metathesis with $[N(PPh_3)_2]Cl$.

Spectroscopic data of interest for the salts of [**3b**]$^-$ are independent of the countercation. Although the alkylidyne (C_α) resonance (δ_C = 256.6) was clearly observed in the $^{13}C\{^1H\}$ NMR spectrum, only one alkynyl resonance (δ_C = 122.5) could be unambiguously identifed, due presumably to this region being cluttered by phenyl and pyrazolyl resonances. The infrared spectrum included absorptions attributable to alkynyl (2005) and carbonyl (1953, 1868 cm^{-1}) groups that are each shifted to lower frequency of those for the neutral complex **2b**, consistent with the anionic nature of the complex. The salt $[Bu_4N]$[**3b**] was structurally characterized, and the key results of this study are summarized in Figure 2, which depicts the molecular geometry of the anion [**3b**]$^-$. The study confirmed the gross formulation as a bis(tricarbido)aurate based on two coordinate gold(I). Examples of simple bis(alkynyl)aurates $[Au(C{\equiv}CR)_2]^-$ (R = CH_2OH,[20] $C_6H_4NO_2$-4,[21] $C_2B_{10}C{\equiv}CH$,[22] C_5H_4N-4,[23] $C({=}CH_2)Me$[24]) that have been structurally characterized with reliable precision[25−27] remain few, in contrast to the more abundant data for neutral derivatives LAuC≡CR. Within this series, C−Au−C angles fall within the narrow range 176.21−178.61° with Au−C bond lengths of 1.951−2.007 Å. These parameters for [**3b**]$^-$ (175.5(7)° and 1.969(15), 1.971(15) Å, respectively) are therefore unremarkable

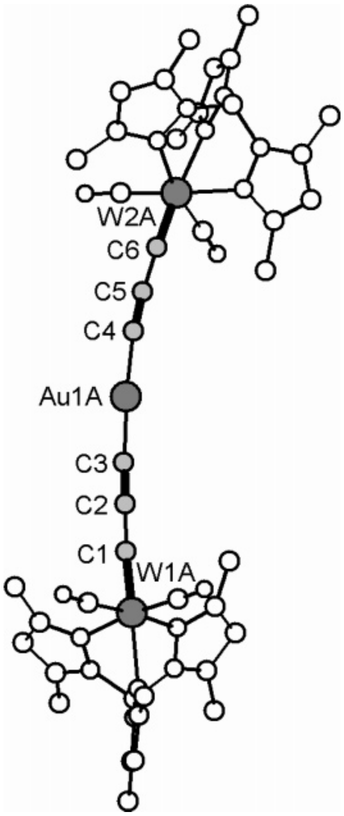


Figure 2. Molecular geometry of the anion [**3b**]$^-$ in a crystal of $[Bu_4N]$[**3b**] (hydrogen atoms omitted; one set of disordered W and Au positions shown; C1 and C6 correspond to C_α; C2 and C5 to C_β; C3 and C4 to C_γ). Selected bond distances (Å) and angles (deg): C1−C2 1.406(19), C1−W1A 1.816(15), C2−C3 1.227(18), C3−Au1A 1.969(15), C4−C5 1.217(18), C4−Au1A 1.970(15), C5−C6 1.402(18), C6−W2A 1.819(15), C7−W1A 1.97(2), N11−W1A 2.198(13), N21−W1A 2.224(11), N31−W1A 2.281(11), N41−W2A 2.305(11), N51−W2A 2.225(12), N61−W2A 2.221(10), C2−C1−W1A 173.1(12), C3−C2−C1 178.7(17), C2−C3−Au1A 174.3(14), C5−C4−Au1A 172.5(16), C4−C5−C6 175.8(19), C5−C6−W2A 169.7(13), C4−Au1A−C3 175.5(7).

---

[17] Dewhurst, R. D.; Hill, A. F.; Rae, A. D.; Willis, A. C. *Organometallics* **2005**, *24*, 4703.

[18] For reviews of the chemistry of alkylidyne complexes: (a) Kim, H.-S.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (b) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227. (c) Mayr, A.; Ahn, S. *Adv. Trans. Metal Coord. Chem.* **1996**, *1*, 1. (d) *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; NATO ASI Series C392; Kluwer: Dordrecht, 1992. (e) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

[19] (a) Nast, R.; Schneller, P.; Hengefeld, A. *J. Organomet. Chem.* **1981**, *214*, 273. (b) Nast, R.; Kirner, U. *Z. Anorg. Allg. Chem.* **1964**, *330*, 311. (c) Vicente; J.; Chicote, M. T. *Coord. Chem. Rev.* **1999**, *193−195*, 1143.

[20] Vicente, J.; Chicote, M.-T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

[21] Vicente, J.; Chicote, M. T.; Brisqueta, M. D.; de Arellano, M. C. R.; Jones, P. G.; Humphrey, M. G.; Cifuentes, M. P.; Samoc, M.; Luther-Davies, B. *Organometallics* **2000**, *19*, 2968.

[22] Vicente, J.; Chicote, M.-T.; Alvarez-Falcon, M. M.; Fox, M. A.; Bautista, D. *Organometallics* **2003**, *22*, 4792.

[23] Ferrer, M.; Rodriguez, L.; Rossell, O.; Pina, F.; Lima, J. C.; M. Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **2003**, *678*, 82.

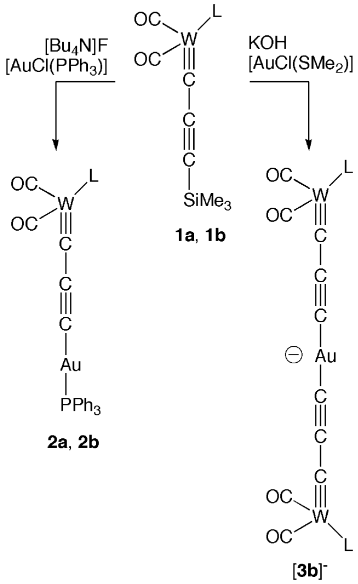
[24] Yam, V. W.-W.; Cheung, K.-L.; Yip, S.-K.; Cheung, K.-K. *J. Organomet. Chem.* **2003**, *681*, 196.

[25] The bis(alkynyl)aurate component of the crystal structures of $[Au_6Pt(C{\equiv}CCMe_3)(PPh_3)_7][Au(C{\equiv}CCMe_3)_2]$[26] and $[Au_3(C{\equiv}CPh)_2(dppm)_2][Au(C{\equiv}CPh)_2]$[27] revealed disorder.

[26] Smith, D. E.; Welch, A. J.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4616.

[27] Che, C.-M.; Yip, H.-K.; Lo, W.-C.; Peng, S.-M. *Polyhedron* **1994**, *13*, 887.

Scheme 2. Synthesis of Tungsten−Gold Tricarbido Complexes: "a" Series L = HB(pz)$_3$, "b" Series L = HB(pz′)$_3$



for such a linkage. Although no single angle along the W1A−W2A chain shows particularly significant deviation from linearity, each is cumulative, culminating in a bowing of the spine such that the two tungsten atoms are 0.213 Å closer than the sum of individual bond lengths along the chain. This bending may be attributed to a general accommodation of the Bu$_4$N cation, although no specific intermolecular interactions are notable. Although [Bu$_4$N][**3b**] is the first structurally characterized example of a bis(metallapolycarbyl)aurate, Bruce has previously reported the synthesis of the bis(diyndiyl) salts [N(PPh$_3$)$_2$][Au{C≡CC≡CML$_n$}$_2$] [ML$_n$ = AuPPh$_3$, W(CO)$_3$(η-C$_5$H$_5$)] from the reaction of [N(PPh$_3$)$_2$][Au(acac)$_2$] with [Au(C≡CC≡CH)(PPh$_3$)] or [W(C≡CC≡CH)(CO)$_3$(η-C$_5$H$_5$)]. The cationic complex [Au{C≡CC≡CCu$_3$(dppm)$_3$I}$_2$]$^+$ was obtained from [N(PPh$_3$)$_2$][Au(C≡CC≡CH)$_2$] and [Cu$_3$(dppm)$_3$I$_2$]I and is presumed to have a core similar to the structurally characterized neutral complex [HC≡CC≡CAu{C≡CC≡CCu$_3$(dppm)$_3$I}$_2$] that arose as a minor side product from an attempted CuI-catalyzed condensation of [Au$_2$Cl$_2$(dppm)] with [Au$_2$(C≡CC≡CH)$_2$(dppm)].[28]

Conclusions

The facility with which [Bu$_4$N][**3a**] is formed as a side product during the ambient temperature synthesis of **2a**, coupled with the ease of synthesis of [N(PPh$_3$)$_2$][**3b**], does perhaps raise mechanistic questions about the active species involved in the transfer of gold-bound alkynyl and metallapolynyl groups. Given that Pd(PPh$_3$)$_4$ and CuI are requisite components of the catalyst,[3b] and the ability of the latter to act as a "phosphine sponge", it may well be that small amounts of anionic bis(alkynyl)aurates are formed and that these are more nucleophilic alkynyl transfer agents than the neutral phosphine precursors.

Experimental Section

General Comments. All manipulations, unless otherwise stated, were carried out under an atmosphere of dinitrogen using conventional Schlenk-line and glovebox techniques. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on Varian Gemini 300 (^{1}H: 300.075 MHz, ^{31}P{^{1}H}: 121.47 MHz) or Varian Mercury 300 (^{1}H: 300.066 MHz, ^{31}P{^{1}H}: 121.469 MHz) spectrometers. ^{13}C{^{1}H} spectra were recorded on Varian INOVA 300 (^{13}C{^{1}H}: 75.421 MHz) or Varian INOVA 500 (^{13}C{^{1}H}: 125.736 MHz) spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts were referenced to the residual solvent peaks. ^{31}P{^{1}H} NMR chemical shifts were reported relative to an external standard (H$_3$PO$_4$). Elemental microanalytical data were obtained from the Research School of Chemistry microanalytical service. Electrospray mass spectrometry (ESI) was performed by the Research School of Chemistry mass spectrometry service. Samples for ESI were prepared by dissolving a solid in a small amount of CH$_2$Cl$_2$ and diluting with either acetonitrile or methanol.

[W(≡CC≡CAuPPh$_3$)(CO)$_2${HB(pz)$_3$}] (2a). A mixture of [W(≡CC≡CSiMe$_3$)(CO)$_2${HB(pz)$_3$}] (**1a**: 200 mg, 0.356 mmol) and [AuCl(PPh$_3$)] (168 mg, 0.340 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with [NBu$_4$]F (0.71 mL, 1.0 M, 0.71 mmol, Aldrich) and stirred overnight. The solution was diluted with ethanol and then slowly concentrated under vacuum, providing a red solid, which was filtered off, rinsed with ethanol and pentane, and dried under vacuum. Yield: 231 mg (73%). IR Nujol: 2009 $\nu_{C≡C}$, 1961, 1869 ν_{CO} cm^{-1}. CH$_2$Cl$_2$: 2012 $\nu_{C≡C}$, 1975, 1887 ν_{CO} cm^{-1}. NMR (CD$_2$Cl$_2$, 25 °C) ^{1}H: δ 8.01 [br s, 3 H, H^3(pz)], 7.71, 7.70 [s × 2, 3 H, H^5(pz)], 7.48−7.56 [m, 15 H, C$_6$H$_5$], 6.27, 6.16 [unresolved t × 2, 3 H, H^4(pz)] ppm. ^{13}C{^{1}H}: δ 255.8 [s + d, $^1J_{WC}$ = 196, W≡C$_\alpha$], 226.4 [s + d, $^1J_{WC}$ = 168, CO], 145.3 (2 C), 144.1 (1 C) [C^5(pz)], 135.9 (1 C), 135.8 (2 C) [C^3(pz)], 134.6 [d, $^2J_{PC}$ = 14.0, C^{2,6}(C$_6$H$_5$)], 132.1 [C^4(C$_6$H$_5$)], 130.0 [obscured d, C^1(C$_6$H$_5$)], 129.5 [d, $^2J_{PC}$ = 11.6, C^{3,5}(C$_6$H$_5$)], 126.8 [br d, $^2J_{PC}$ = 129 Hz, C≡C_γ-Au], 121.3 [unresolved d, C_β≡C−Au], 106.2 (2 C), 106.0 (1 C) [C^4(pz)] ppm. ^{31}P{^{1}H}: δ 42.3 ppm. MS (ESI): *m/z* (%) 1407 (38) [M + Au(PPh$_3$)]$^+$, 947 (<1) [M]$^+$, 721 (78) [Au(PPh$_3$)$_2$]$^+$, 500 (100) [Au(MeCN)(PPh$_3$)]$^+$. Anal. Found: C 40.61, H 2.77, N 8.45. Calcd for C$_{32}$H$_{25}$AuBN$_6$O$_2$PW: C 40.54, H 2.66, N 8.86.

[W(≡CC≡CAuPPh$_3$)(CO)$_2${HB(pz′)$_3$}] (2b). A mixture of [W(≡CC≡CSiMe$_3$)(CO)$_2${HB(pz′)$_3$}] (**1b**: 100 mg, 0.155 mmol) and [AuCl(PPh$_3$)] (69 mg, 0.140 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with [NBu$_4$]F (0.31 mL, 1.0 M, 0.31 mmol, Aldrich) and stirred for 3 h. The solution was diluted with ethanol and concentrated under vacuum to provide a red solid, which was filtered off, rinsed with ethanol, and dried under vacuum. Yield: 104 mg (72%). IR Nujol: 2014 $\nu_{C≡C}$, 1957, 1864 ν_{CO} cm^{-1}. CH$_2$Cl$_2$: 2014 $\nu_{C≡C}$, 1967, 1878 ν_{CO} cm^{-1}. NMR (CD$_2$Cl$_2$, 25 °C) ^{1}H: δ 7.52 [m, 15 H, C$_6$H$_5$], 5.94, 5.80 [s × 2, 3 H, H^4(pz)], 2.60 (6 H), 2.39 (9 H), 2.34 (3 H) [s × 3, 18 H, H^3(pz)] ppm. ^{13}C{^{1}H}: δ 251.7 [s, W≡C$_\alpha$], 226.4 [s + d, $^1J_{WC}$ = 164, CO], 152.6 (3 C) [C^5(pz)], 145.8 (1 C), 145.1 (2 C) [C^3(pz)], 134.6 [d, $^2J_{PC}$ = 13.1, C^{2,6}(C$_6$H$_5$)], 132.0 [C^4(C$_6$H$_5$)], 130.0 [obscured d, C^1(C$_6$H$_5$)], 129.5 [d, $^2J_{PC}$ = 10.7, C^{3,5}(C$_6$H$_5$)], 125.2 [br d, $^2J_{PC}$ = 143 Hz, C≡C_γ-Au], 121.0 [br s, C_β≡C−Au], 106.7 (1 C), 106.6 (2 C) [C^4(pz)], 16.5 (2 C), 15.3 (1 C) [C^{5}Me(pz)], 12.7 [C^{3}Me(pz)] ppm. ^{31}P{^{1}H}: δ 42.4 ppm. MS (ESI): *m/z* (%) 1045 (2) [M − CO + MeCN]$^+$, 1032 (8) [M]$^+$, 1004 (3) [M − CO]$^+$, 977 (2) [M − 2CO]$^+$. Anal. Found: C 44.55, H 3.91, N 8.04. Calcd for C$_{38}$H$_{37}$AuBN$_6$O$_2$PW: C 44.21, H 3.61, N 8.14. *Crystal data for* **2b**: C$_{38}$H$_{37}$AuBN$_6$O$_2$PW, M_w = 1032.33, monoclinic, $P2_1/c$, $a = 9.557(2)$ Å, $b = 13.989(3)$ Å, $c = 29.553(6)$ Å, $\beta = 98.41(3)°$, $V = 3908.5(14)$ Å, $Z = 4$, μ(Mo Kα) = 6.771 mm^{-1}, $D_{calc} = 1.754$ Mg m^{-3}, $T = 200(2)$ K, red rod, 8944 independent measured reflections, $R_1 = 0.0391$, $wR_2 = 0.0936$, 6392 absorption-corrected reflections [$I > 2\sigma(I)$, $2\theta \le 55°$], 460 parameters, CCDC 273886.

---

[28] Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Smith, M. E.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 995.

$[N(PPh_3)_2]$ $[Au(C{\equiv}CC{\equiv}W(CO)_2\{HB(pz')_3\})_2]$ ($[N(PPh_3)_2]$[3b]). To potassium hydroxide (two pellets, 206 mg, 3.67 mmol) in methanol (20 mL) was added $[W({\equiv}C-C{\equiv}C-SiMe_3)(CO)_2\{HB(pz')_3\}]$ (**1b**: 300 mg, 0.456 mmol), and the mixture stirred for 5 min. To this was added $[AuCl(SMe_2)]$ (60 mg, 0.20 mmol), and stirring was maintained for 3 h. Then the mixture was filtered through diatomaceous earth. To the filtrate was added bis(triphenylphosphoranylidene)ammonium chloride (132 mg, 0.230 mmol), and the resulting orange precipitate was filtered off, washed with methanol and then petroleum ether, and dried under vacuum. Yield: 319 mg (73%, dihydrate). IR Nujol: 1998 $\nu_{C{\equiv}C}$, 1943, 1855 ν_{CO} cm^{-1}. CH_2Cl_2: 2005 $\nu_{C{\equiv}C}$, 1953, 1868 ν_{CO} cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 7.63, 7.51 [m × 2, 30 H, C_6H_5], 5.75, 5.65 [s × 2, 6 H, H^4(pz)], 2.50 (12 H), 2.31 (6 H), 2.30 (12 H), 2.26 (6 H) [s × 4, 36 H, CH_3] ppm. $^{13}C\{^1H\}$: δ 256.6 [$W{\equiv}C_\alpha$], 227.3 [CO], 152.4 (4 C), 151.7 (2 C) [C^5(pz)], 144.4 (2 C), 143.6 (4 C) [C^3(pz)], 133.8 [$C^4(C_6H_5)$], 132.1 [d, J_{PC} = 12.2, $C^{2,6}$ or $C^{3,5}(C_6H_5)$], 129.7 [d, J_{PC} = 13.8, $C^{2,6}$ or $C^{3,5}(C_6H_5)$], 126.9 [d, $^1J_{PC}$ = 106.6 Hz, $C^1(C_6H_5)$], 122.5 [$C_\beta{\equiv}C-Au$ or $C{\equiv}C_\gamma$-Au], 106.0 [C^4(pz)], 16.5 (4 C), 15.1 (2 C) [C^5Me(pz)], 12.6 (6 C) [C^3Me(pz)] ppm. $^{31}P\{^1H\}$: δ 21.9 ppm. MS (ESI): *m/z* (%) = 1343 (78) $[M]^-$, 796 (100) $[W(CCCAu)(NCMe)_2\{HB(pz')_3\}]^-$. Anal. Found: C, 47.59; H, 4.01; N, 9.58. Calcd for $C_{76}H_{74}AuB_2N_{13}O_4P_2W_2{\cdot}2(H_2O)$: C, 47.60; H, 4.10; N, 9.49. Presence of two H_2O molecules confirmed by integration of ^1H NMR spectrum and could not be removed even with prolonged drying. *Crystal data for* $[Bu_4N]$[**2b**]: $C_{56}H_{83}AuB_2N_{13}O_4W_2$, M_w = 1588.64, monoclinic, $P2_1/n$, a = 19.161(5) Å, b = 10.128(5) Å, c = 32.897(5) Å, β = 95.063(5)°, V = 6359(4) Å^3, Z = 4, μ(Mo Kα) = 5.963 mm^{-1}, D_{calc} = 1.659 Mg m^{-3}, T = 200(2) K, red rod, 11 195 independent measured reflections, R_1 = 0.0688, wR_2 = 0.1475, 7017 absorption-corrected reflections [$I > 2\sigma(I)$, $2\theta \leq 50.4°$], 757 parameters, CCDC 275211. The refinement was based on a model involving position disorder of tungsten and gold sites, details of which are given in the CIF file (Supporting Information).

Supporting Information Available: Full details of the crystal structure determinations of **2b** (CCDC 273886) and $[Bu_4N]$[**3b**] (CCDC 275211) in Crystallographic Information File format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050528I