JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

A Golden Ring: Molecular Gold Carbido Complexes

Elliot S. Borren, Anthony F. Hill,* Rong Shang, Manab Sharma, and Anthony C. Willis

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

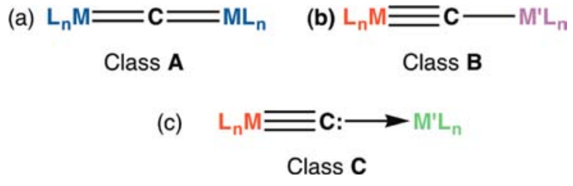
S *Supporting Information*

ABSTRACT: Stannylcarbynes $[M(\equiv CSnMe_3)(CO)_2(Tp^*)]$ [M = Mo, W; Tp* = hydrotris(dimethylpyrazol-1-yl)borate], which are readily obtained via the successive treatment of $[M(\equiv CBr)(CO)_2(Tp^*)]$ with ^nBuLi and $ClSnMe_3$, serve as effective carbyne transmetalation agents for the preparation of heteronuclear molecular gold carbido complexes such as $[M(\equiv CAuPPh_3)(CO)_2(Tp^*)]$ and the tetrameric golden ring complex $[W(\equiv CAu)(CO)_2(Tp^*)]_4$, which are in turn able to transfer the carbido unit to palladium.

Molecular carbido complexes take three distinct forms. The oldest involve interstitial carbido atoms within clusters.[1] Until recently, these carbon atoms have played little more than a structural cementing role, being buried within polymetallic assemblies and shielded from *direct* participation in chemical transformations. This perspective may change now that a carbido atom has been implicated in the FeMo-cofactor core of nitrogenase.[2] At the other extreme, the isolation of terminal carbido complexes might be expected to presage a rich chemistry were it not for the somewhat unexpectedly reticent reactivity of such species.[3] Between these extremes, binuclear carbido complexes present an intermediate situation for exploration.

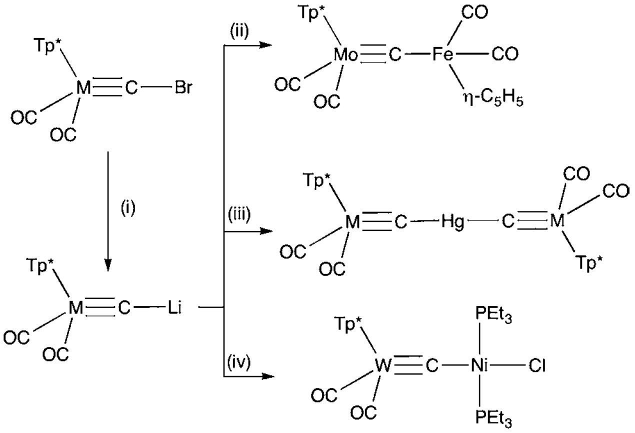
The few examples known to date may be described by two limiting valence-bond descriptions (Scheme 1): (i) dimetallacumulenes (class A),[4,5] as exemplified by Mansuy's archetypal porphyrin systems,[4] where an Fe═C═Fe bonding description has some merit, and (ii) metallacarbynes (class B), which involve electronically disparate metals and call for a localized valence-bond description (M≡C–M′).[6] A third class (C), examples of which remain rare,[3b] involves the reversible formation of a weak, labile adduct between a terminal carbido ligand and an unsaturated metal center. An analogy with CO, isonitrile, or N-heterocyclic carbene coordination may be entertained, leading to their description as dative or polar covalent bonds (M≡C:→M′). No doubt, intermediate examples will emerge with time to interpolate a bonding continuum.

Scheme 1. Classification of Binuclear Carbido Ligands: (a) Cumulenic (Class A); (b) Metallacarbyne (Class B); (c) Polar Covalent (Class C)



We recently investigated the reactions of lithiated carbyne complexes $[M\{\equiv CLi(THF)_n\}(CO)_2(Tp^*)]$ [M = Mo, W; Tp* = κ^3-hydrotris(3,5-dimethylpyrazol-1-yl)borate] with a variety of electrophiles, which lead to novel heteroatom C-functionalized carbyne derivatives,[6e,f,8] including ones with substituents less amenable to conventional carbyne synthetic protocols.[7] Among these, the reactions with transition-metal electrophiles provide a remarkably facile route to heterobimetallic bridging carbido complexes of class B in which the second metal is d^6 iron,[8d] d^8 nickel,[8e] or d^{10} mercury (Scheme 2).[6f] Caveats associated with the generation, thermolability, and longevity of the intermediate lithiated carbynes encouraged us to pursue more readily manageable reagents for the installation of carbido groups. To this end, we considered the possibility of preparing stannyl- or gold-functionalized carbyne complexes.

Scheme 2. Synthesis of Heterobimetallic Carbido Complexes via Halocarbyne Lithium/Halogen Exchange[a]

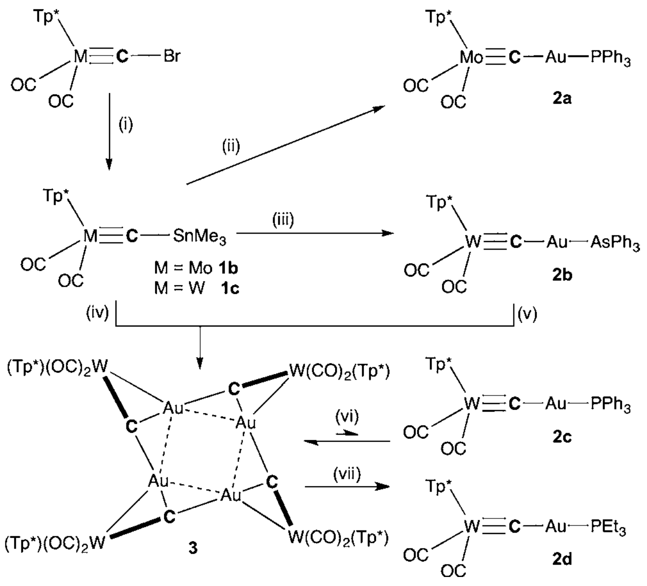


[a]Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate).[6f,8d,e] Conditions: (i) ^nBuLi, −78 °C, THF; (ii) $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$; (iii) $HgCl_2$; (iv) $[NiCl_2(PEt_3)_2]$.

The stannylcarbyne complex $[Mo(\equiv CSnPh_3)(CO)_2(Tp^*)]$ (**1a**) results from the successive treatment of $[Mo(\equiv CBr)(CO)_2(Tp^*)]$ with ^nBuLi and $ClSnPh_3$.[8b] Here we report that the complexes $[M(\equiv CSnMe_3)(CO)_2(Tp^*)]$ [M = Mo (**1b**), W (**1c**)] may be prepared similarly and in high yield by employing $ClSnMe_3$ (Scheme 3). The complexes are thermally stable and only mildly air-sensitive in solution. Characterization data [see

Received: January 25, 2013
Published: March 13, 2013

Scheme 3. Synthesis of Heteronuclear Gold Carbido Complexes[a]



[a]Conditions: (i) ${}^nBuLi$, $ClSnMe_3$; (ii) $[AuCl(PPh_3)]$; (iii) $[AuCl(AsPh_3)]$; (iv) $[AuCl(SMe_2)]$; (v) 25 °C, 12 h; (vi) PPh_3; (vii) PEt_3.

the Supporting Information (SI)] correspond to those for the structurally authenticated analogue **1a** and call for no further comment other than to note that the ^{13}C resonances for the carbyne carbons display coupling to the spin-active isotopes of tin (e.g., for **1c**: $\delta_C = 343.4$ ppm, $^1J_{CSn} = 241.4$ Hz, $^1J_{CW} = 63.4$ Hz).

Organotin reagents have on a few isolated occasions been shown to undergo transmetalation reactions with $[AuCl(PPh_3)]$ to afford organogold derivatives.[9] We therefore investigated the reaction of **1b** with $[AuCl(PPh_3)]$ in benzene at room temperature and found that it cleanly provides the novel yellow mononuclear gold class-B carbido complex $[Mo(\equiv CAuPPh_3)(CO)_2(Tp^*)]$ (**2a**). The formulation of **2a** rests firmly on spectroscopic data, which included the observation of a molecular ion using electrospray ionization (ESI) mass spectrometry. Unfortunately, the low solubility of **2a** precluded the unequivocal observation of the ^{13}C resonance associated with the bridging carbido ligand. The complex slowly decomposes at room temperature, depositing colloidal gold, thereby thwarting attempts to obtain useful microanalytical and crystallographic data.

In search of more stable analogues of **2a**, the reaction of **1c** with $[AuCl(AsPh_3)]$ was investigated, but rather than the anticipated analogue $[W(\equiv CAuAsPh_3)(CO)_2(Tp^*)]$ (**2b**), which could only be observed fleetingly ($\nu_{CO} = 1998$, 1915 cm^{-1} in CH_2Cl_2), a red compound devoid of any coordinated arsine, **3**, was isolated. In view of the conspicuous absence of the original gold coligand, the more labile reagent $[AuCl(SMe_2)]$ was treated with **1c** and also found to provide **3** in comparable yield (84%). The solution spectroscopic data were consistent with the empirical formulation "$[W(\equiv CAu)(CO)_2(Tp^*)]_n$", with only single resonances being observed for the carbido ligand ($\delta_C = 361.3$ ppm, $^1J_{CW} = 75.5$ Hz) and the carbonyl ligands ($\delta_C = 222.6$ ppm, $^1J_{CW} = 181.1$ Hz) in C_6D_6. The pattern of resonances for the Tp* ligand indicated local C_s symmetry (on the ^1H and ^{13}C NMR time scales) for the tungsten center(s), while the high-resolution ESI mass spectrum suggested a tetrameric assembly.

The tetrameric nature of the complex was confirmed by an X-ray diffraction study, the results of which are summarized in Figure 1.[10]

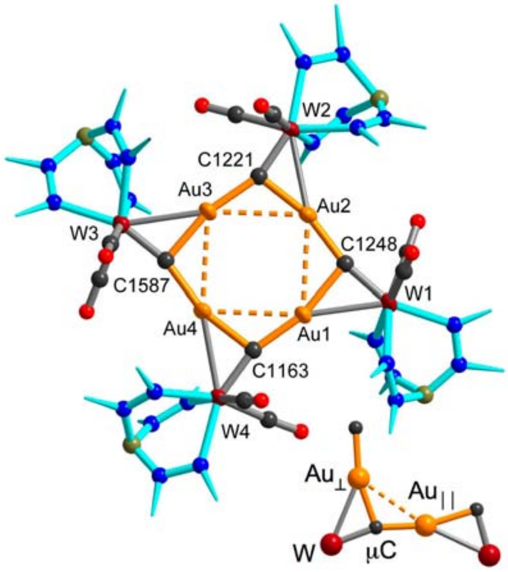
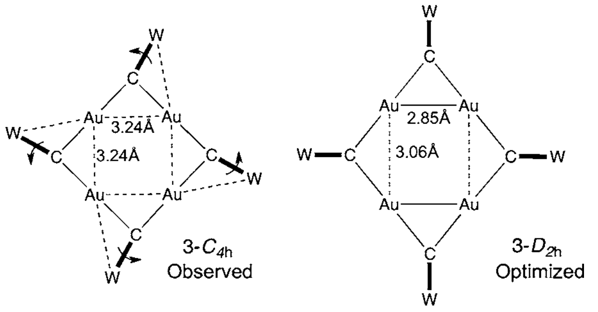


Figure 1. Molecular structure of **3** in a crystal (60% displacement ellipsoids, Tp* ligands simplified for clarity). Selected mean bond lengths (Å) and angles (deg): $Au_\perp$–W, 2.8322; $Au_\parallel$–μC, 1.995; $Au_\perp$–μC, 2.078; W–μC, 1.877; $Au_\perp \cdots Au_\parallel$, 3.231; W–$Au_\perp$–$Au_\parallel$, 167.8; W–$\mu$C–$Au_\parallel$, 163.4; W–$\mu$C–$Au_\perp$, 92.1.

The crystallographic symmetry ($P\bar{1}$) does not impose any geometric constraints upon the molecule such that each metric parameter is unique. Accordingly, this discussion is limited to mean geometric parameters. The central core comprises an eight-membered $(AuC)_4$ ring bearing four tangential tungsten centers. The mean Au···Au separation of 3.231 Å lies toward the long end of the range for which aurophilic interactions[11] might normally be invoked but is still within the sum of the van der Waals radii (ca. 3.6 Å). Each carbido bridge adopts T-shaped coordination by interacting differently with two gold centers, one ($Au_\parallel$) approaching collinearity with the W–μC vector (mean W–μ-C–$Au_\parallel$ angle = 163.4°) and the other ($Au_\perp$) close to orthogonal to this vector (mean W–μ-C–$Au_\perp$ angle = 92.1°). The W–μC separation of 1.877 Å remains within the range typical of W≡C multiple bonds,[7a] while the W–Au separation (2.8322 Å) and large W–μ-C–$Au_\parallel$ angle are reminiscent of the rare examples of "semibridging" carbyne ligands, for which one previous tungsten–gold example has been reported, namely, $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (W–C–C = 162.77°, W–Au = 2.781 Å, W–C–Au = 86°).[12] An alternative perspective for interpreting the structure of **3** might consider the isolobal mapping that relates W≡C and C≡C triple bonds, in which case parallels with gold alkynyls may be entertained. Notably, the molecular structure of **3** corresponds in isolobal terms to that suggested by Coates for oligomeric $(AuCC^tBu)_n$,[13] which has eluded observation in the intervening 50 years. A compound of the same empirical formula was subsequently identified by Mingos as the [2]catenane $[(AuCC^tBu)_6]_2$.[14] The structural chemistry of binary gold acetylides $(RCCAu)_n$ remains poorly studied, in part because of their oligomeric (and explosive!) nature. This arises from the combination of strong Au–C σ bonding with weaker, labile Au(CC) π and aurophilic Au···Au interactions, which do not persist when stronger extraneous donors are available to sustain disaggregation.

Complex **3** displays no fluorescence of note, but the adopted structure clearly has intergold separations (3.32 Å) less than twice the van der Waals radius for gold. The question of direct Au···Au interactions therefore arose and was addressed by a computational study at the ONIOM(MO6:PM6) DFT level of theory (see the SI for details). Interestingly, attempts to optimize the geometry of **3** beginning from the experimentally determined atomic coordinates resulted in a significant change in both the geometry and bonding. This suggests that the observed geometry (an approximately C_{4h} $W_4Au_4C_4$ core; Chart 1) is imposed by the crystal lattice, while the ground-state geometry in solution is likely to be that shown in Figure 2 (**3-*D*$_{2h}$**). Notably, the less compact **3-*D*$_{2h}$** geometry involves symmetrical carbido bridges with *no direct gold–tungsten interaction* and substantially contracted Au···Au separations, which are however not identical (2.86 and 3.06 Å). Among the derived frontier molecular orbitals (MOs) associated with the rectangular core of **3-*D*$_{2h}$**, the HOMO−5 involves alternating bonding and antibonding interactions around the Au_4 ring, to which we attribute the significant alternation in Au···Au bond-lengths (Figure 2).

Chart 1. Idealized Geometries for Experimentally Observed Semibridging (3-*C*$_{4h}$) and Computationally Optimized Symmetrically Bridging (3-*D*$_{2h}$) Carbido Complexes



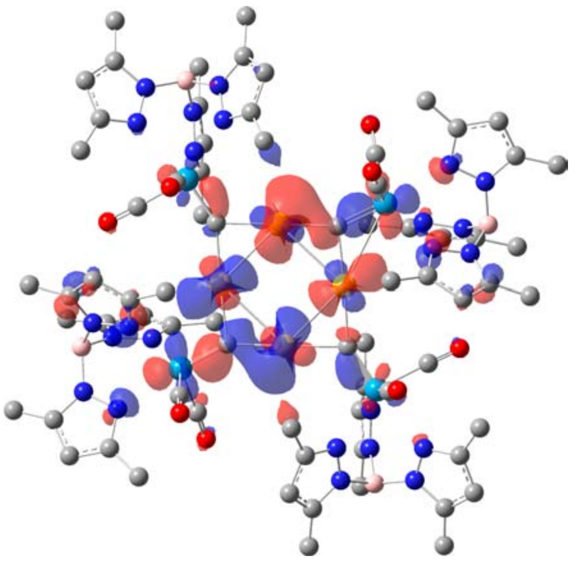


Figure 2. ONIOM(MO6:PM6)-optimized geometry of **3** in the gas phase (**3-*D*$_{2h}$**), with an overlay of the **3-*D*$_{2h}$** HOMO−5.

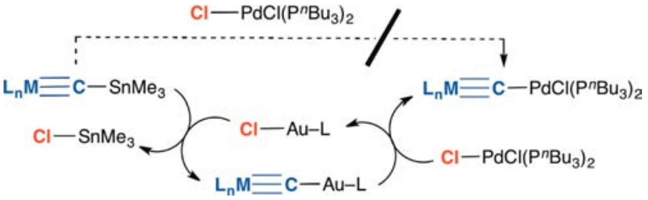
Because geometry optimization led from the observed geometry to **3-*D*$_{2h}$**, it was necessary to derive MOs from a single-point calculation based on the **3-*C*$_{4h}$** coordinates (see the SI). Natural bond orbital (NBO) analysis indicated a triple bond (one σ bond and two π bonds) within each W≡C unit. The σ bonds comprise ~40% tungsten (~69% d character) and ~60% carbon (sp character) contributions. The WC π bond in the C_4Au_4 plane has noticeably more tungsten character than the one orthogonal to the metallacycle (ca. 65 and 45%, respectively, both with >90% d character). The WC–Au bond is formed by a ~75% C(sp) contribution with the Au 6s orbital. Interestingly, a strong donor–acceptor interaction between one WC π-bond pair and a Au 6p orbital (>95%) appears to be primarily responsible for the orthogonal C–Au bond formation. There is, however, no evidence of direct Au···Au interactions among the Au atoms in the central core, consistent with the absence of emission spectra for **3** during luminescence studies. Previous examples of metal–carbon multiple bonds coordinating to gold(I) include the salts $[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$[16] and $[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4Cl_2(bipy)_2][PF_6]$[16b] and the μ-methylene complex $[OsAu(\mu\text{-}CH_2)ClI(NO)(PPh_3)_2]$.[17]

The symmetrically bridging carbido ligand suggested to occur for **3-*D*$_{2h}$** in solution is noteworthy in that three-coordinate carbido bridging is limited to a single example in the platinum–diruthenium compound $[(Cp^*Ru)_2(\mu_2\text{-}H)(\mu_2\text{-}NHPh)(\mu_3\text{-}C)Pt(CH_3)(PMe_3)_2]OTf$ recently reported by Matsuzaka,[15] which results from activation of a bridging methylene ligand. However, the bonding is quite distinct from that observed for **3-*D*$_{2h}$**, as the Pt–C bond is essentially a single bond and the unsaturation is associated with the $Ru_2(\mu\text{-}C)$ unit.

Given that **3** forms via dissociation of $AsPh_3$ from the observable complex **2b** or SMe_2 from the putative intermediate $[W(\equiv CAuSMe_2)(CO)_2(Tp^*)]$, we briefly considered whether **3** might be disaggregated by more nucleophilic ligands. While treating **3** with PPh_3 failed to generate observable amounts of **2c** (the tungsten analogue of **2a**) *directly*, we may infer from the broadening of the ^{31}P NMR peak for "free" triphenylphosphine that an equilibrium between **3** and **2c** operates in solution. The more nucleophilic phosphine PEt_3, however, cleanly reacts with **3** to provide the monomeric carbido complex $[W(\equiv CAuPEt_3)(CO)_2(Tp^*)]$ (**2d**). These results are consistent with the relative labilities of these ligands when bound to Au(I) centers: $PEt_3 < PPh_3 < AsPh_3 < SMe_2$.

Cross demonstrated the versatility of gold alkynyls for organotransmetalation to palladium,[18] and more recently, Bruce showed that this transmetalation may be productively incorporated into catalytic processes for C–C bond formation.[19] Transmetalation also occurs between isolated **3** and $[PdCl_2(P^nBu_3)_2]$ to afford the new palladium carbido complex *trans*-$[Pd\{C\equiv W(CO)_2(Tp^*)\}Cl(P^nBu_3)_2]$ (**4**) (Scheme 4). Given the clean formation of **3** from **1c** and subsequent

Scheme 4. Carbido Relay Transmetalation from Tin to Palladium via Gold



transmetalation to give **4**[20] and "AuCl", we considered whether a relay transmetalation between **1** and palladium via gold might be viable. While the generality of this approach has yet to be established, the proof of concept follows from a model study: complex **1c** failed to react with $[PdCl_2(P^nBu_3)_2]$ at room temperature over a period of 7 days, but addition of either $[AuCl(AsPh_3)]$ or $[AuCl(SMe_2)]$ (5 mol %) resulted in the smooth conversion of **1c** to **4** (Scheme 4).[21]

While it would be premature to extrapolate from a single result, the implication is that transmetalation from tin to palladium does not occur at room temperature but transfer from tin to gold and then from gold to palladium is productive under these mild conditions. In addition to providing novel bridging modes for carbido ligands, the utility of these gold carbido reagents could be demonstrated with respect to participation in facile transmetalation processes with metal halides, which we are currently exploring. We note that the beneficial effect of cuprous salts on Stille couplings is well-documented[22] and now suggest that suitable gold complexes may well play a useful cofactor role that is worthy of further exploration.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **3** (CCDC898193) in CIF format, synthetic and spectroscopic data for reported compounds, and details of computational studies of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

a.hill@anu.edu.au

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Australian Research Council (DP0557815 and DP1093516). The authors are grateful to the National Computational Infrastructure (Y49) for access to the Australian National University supercomputer facilities and the Tasmanian Partnership of Advanced Computing.

■ REFERENCES

(1) (a) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 301. (b) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1.

(2) Markus, M. G.; Schneider, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 2.

(3) (a) Carlson, R. G.; Gile, M. A.; Heppert, J. A.; Mason, M. H.; Powell, D. R.; Velde, D. V.; Vilain, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 1580. (b) Hejl, A.; Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Chem. Commun.* **2002**, 2524. (c) Caskey, S. R.; Stewart, M. H.; Kivela, J. E.; Sootsman, J. R.; Johnson, M. J. A.; Kampf, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 16750. (d) Stewart, M. H.; Johnson, M. J. A.; Kampf, J. W. *Organometallics* **2007**, *26*, 5102. (e) Mutoh, Y.; Kozono, N.; Araki, M.; Tsuchida, N.; Takano, K.; Ishii, Y. *Organometallics* **2010**, *29*, 519.

(4) (a) Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681. (b) Mansuy, D.; Lecomte, J.-P.; Chottard, J.-C.; Bartoli, J.-F. *Inorg. Chem.* **1981**, *20*, 3119.

(5) (a) Miller, R. L.; Wolczanski, P. T.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 10422. (b) Beck, W.; Knauer, W.; Robl, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 318. (c) Solari, E.; Antonijevic, S.; Gauthier, S.; Scopelliti, R.; Severin, K. *Eur. J. Inorg. Chem.* **2007**, 367. (d) Young, R. D.; Hill, A. F.; Cavigliasso, G. E.; Stranger, R. *Angew. Chem. Int. Ed.* **2013**, *52*, 3699.

(6) (a) Latesky, S. L.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 4731. (b) Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324. (c) Knauer, W.; Beck, W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2241. (d) Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414. (e) Cade, I. A.; Hill, A. F.; McQueen, C. M. A. *Organometallics* **2009**, *28*, 6639. (f) Colebatch, A. L.; Cordiner, R. L.; Hill, A. F.; Nguyen, K. T. H. D.; Shang, R.; Willis, A. C. *Organometallics* **2009**, *28*, 4394.

(7) For reviews of carbyne chemistry, see: (a) Caldwell, L. M. *Adv. Organomet. Chem.* **2008**, *56*, 1. (b) Herndon, J. W. *Coord. Chem. Rev.* **2007**, *251*, 1158. (c) Herndon, J. W. *Coord. Chem. Rev.* **2003**, *243*, 3. (d) Herndon, J. W. *Coord. Chem. Rev.* **2001**, *214*, 215. (e) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227. (f) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51.

(8) (a) Hill, A. F.; Shang, R.; Willis, A. C. *Organometallics* **2011**, *30*, 3237. (b) Cordiner, R. L.; Hill, A. F.; Shang, R.; Willis, A. C. *Organometallics* **2011**, *30*, 139. (c) Colebatch, A. L.; Hill, A. F.; Shang, R.; Willis, A. C. *Organometallics* **2010**, *29*, 6482. (d) Cordiner, R. L.; Hill, A. F.; Wagler, J. *Organometallics* **2008**, *27*, 5177. (e) Hill, A. F.; Sharma, M. *Organometallics* **2012**, *31*, 2538.

(9) (a) Gamasa, M. P.; Gimeno, J.; Godefroy, I.; Lastra, E.; Martin-Vaca, B. M.; Garcia-Granda, S.; Gutierrez-Rodriguez, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1901. (b) Meyer, N.; Lehmann, C. W.; Lee, T. K. M.; Rust, J.; Yam, V. W. W.; Mohr, F. *Organometallics* **2009**, *28*, 2931. (c) Meyer, N.; Sivanathan, S.; Mohr, F. *J. Organomet. Chem.* **2011**, *696*, 1244.

(10) Crystal data for **3**: $C_{72}H_{88}Au_4B_4N_{24}O_8W_4{\cdot}H_2O$, MW = 3002.17, triclinic, $P\bar{1}$ (No. 2), $a = 14.1428(4)$ Å; $b = 19.4442(4)$ Å; $c = 19.5444(3)$ Å; $\alpha = 89.6316(13)°$; $\beta = 70.6096(13)°$; $\gamma = 85.4020(12)°$; $V = 5052.3(2)$ Å^3, $Z = 2$, $F_{000} = 2784$, $D_{calcd} = 1.972$ Mg/m^3, μ(Mo Kα) = 10.374 mm^{-1}, $T = 200(2)$ K, brown plate 0.044 mm × 0.160 mm × 0.210 mm, 17 735 independent reflections, F^2 refinement, $R_1 = 0.0724$, $wR_2 = 0.1947$ for 13 065 absorption-corrected reflections with $I > 2\sigma(I)$, $2\theta_{max} = 50°$, 551 parameters, 110 restraints, CCDC 874317. One peripheral pyrazolyl group failed to refine freely to a chemically reasonable geometry and was therefore refined as a rigid group with constrained geometrical parameters reflecting those for the remaining 11 pyrazolyl groups.

(11) Schmidbaur, H.; Cronje, S.; Djordjevic, B.; Schuster, O. *Chem. Phys.* **2005**, *311*, 151.

(12) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 61.

(13) Coates, G. E.; Parkin, C. *J. Chem. Soc.* **1962**, 3220.

(14) Mingos, D. M. P.; Yau, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1894.

(15) Takemoto, S.; Morita, H.; Karitani, K.; Fujiwara, H.; Matsuzaka, H. *J. Am. Chem. Soc.* **2009**, *131*, 18026.

(16) Carriedo, G. A.; Howard, J. A. K.; Marsden, K.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 1589. (b) Carriedo, G. A.; Riera, V.; Sanchez, G.; Solans, X.; Labrador, M. *J. Organomet. Chem.* **1990**, *391*, 431.

(17) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939.

(18) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987 and references therein.

(19) (a) Khairul, W. M.; Fox, M. A.; Zaitseva, N. N.; Gaudio, M.; Yufit, D. S.; Skelton, B. W.; White, A. H.; Howard, J. A. K.; Bruce, M. I.; Low, P. J. *Dalton Trans.* **2009**, 610 and references therein. (b) Antonova, A. B.; Bruce, M. I.; Ellis, B. G.; Gaudio, M.; Humphrey, P. A.; Jevric, M.; Nicholson, B. K.; Perkins, G. J.; Skelton, B. W.; Stapleton, B.; White, A. H.; Zaitseva, N. N. *Chem. Commun.* **2004**, 960.

(20) Transfer of the "$CMo(CO)_2(Tp^*)$" group from Hg to Rh is implicit in the Rh-catalyzed demercuration of $Hg[CMo(CO)_2(Tp^*)]_2$ by $[RhCl(CO)(PPh_3)_2]$ to provide the ethandiylidyne complex (μ-C_2)$[Mo(CO)_2(Tp^*)]_2$.[6f]

(21) The analogous nickel complex $[Ni\{C{\equiv}W(CO)_2(Tp^*)\}Cl(PEt_3)_2]$ has recently been reported.[8e]

(22) (a) Liebeskind, L. S.; Fengi, R. W. *J. Org. Chem.* **1990**, *55*, 5359. (b) Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905. (c) Casado, A. L.; Espinet, P. *Organometallics* **2003**, *22*, 1305. (d) Han, X.; Stolz, B. M.; Corey, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 7600.