modynamic cycle of eqs 1-5 (s = solution, c = crystal, g = gas). In essence, eq 5 describes the metal–arene bond disruption process in *solution*, where $Ln^{\circ}_{(g)}$ is taken to be "unsolvated" (the enthalpy required to strip both arene ligands from the metal to form a "bare", electronically relaxed metal atom).[13] Furthermore, the heats of solution of the $Ln(TTB)_2$ complexes in toluene are expected[3,4,8] to be small and constant and to approximately cancel that of 2TTB in toluene.[14]

$$Ln(TTB)_{2(s)} + {}^{3}\!/_{2}I_{2(s)} \rightarrow LnI_{3(c)} + 2TTB_{(s)} \qquad \Delta H_{rxn} \qquad (1)$$

$${}^{3}\!/_{2}I_{2(c)} \rightarrow {}^{3}\!/_{2}I_{2(s)} \qquad {}^{3}\!/_{2}\Delta H_{soln} \qquad (2)$$

$$LnI_{3(c)} \rightarrow Ln^{\circ}_{(c)} + {}^{3}\!/_{2}I_{2(c)} \qquad -\Delta H_f^{\circ} \qquad (3)$$

$$Ln^{\circ}_{(c)} \rightarrow Ln^{\circ}_{(g)} \qquad \Delta H^{\circ}_{sub} \qquad (4)$$

$$Ln(TTB)_{2(s)} \rightarrow Ln^{\circ}_{(g)} + 2TTB_{(s)} \qquad 2D(Ln\text{-}TTB) \qquad (5)$$

Thermochemical data for the present $Ln(TTB)_2$ complexes are compiled in Table I, where derived *D*(Ln-TTB) data are compared to published results[7d] for group 6 arene sandwich complexes. It is evident that the zero-valent lanthanide-to-arene bonding is very strong—up to 30 kcal/mol greater than that in archetypical $Cr(C_6H_6)_2$ and, in some cases, as strong as metal–arene bonding involving a third row metal (W). Regarding $Ln(TTB)_2$ electronic structure, it has been previously suggested that the lanthanide 5d (Y 4d) orbitals are likely an important factor in the metal–ligand bonding and that, for approximately constant metal radius, lanthanide bis(arene) thermal stabilities qualitatively correlate with the energetic demands of $f^ns^2 \rightarrow f^{n-1}d^1s^2$ promotion.[6b] The present results add quantitative substance to this argument in that the large *D*(GdTTB) value parallels the ease of $f^ns^2 \rightarrow f^{n-1}d^1s^2$ promotion (Gd ≫ Ho ≥ Er ≈ Dy; Gd° has a $4f^75d^16s^2$ ground state).[15] Similarly, Y° has a $4d^15s^2$ ground state.[6b,15] A qualitative similarity of $Ln(TTB)_2$ metal–ligand bonding to that of group 6 is seen in the adherence of the present data to a previously noted correlation[7c] of D(M–arene) data with cohesive energetics for the corresponding bulk metals (Figure 1A). Finally, the combination of sizable *D*(LnTTB) and modest ΔH_{sub}(Ln) values in comparison to the group 6 analogues leads to the interesting observation (Figure 1B) that the reaction of *bulk* lanthanide metals with TTB is calculated to be *exothermic*, in contrast to group 6.

The present quantitation of lanthanide–arene bond enthalpies in the zero-valent sandwich complexes argues for an unprecedented organolanthanide bonding mode. Additionally, the present data raise interesting bonding energetic questions about other arene ligands and related zero-valent early metals as well as about the quantitative aspects of the electronic structure. These issues are presently being addressed.

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[13] (a) This approach is preferable to attempted calculation of gas-phase D(LnTTB) parameters which would require presently unavailable and difficultly measured $Ln(TTB)_2$ heats of sublimation. Moreover, most chemistry of interest occurs in the solution phase. In cases where corrections to the gas phase have been performed, results are in satisfactory agreement with nonpolar solution phase data.[7a,8,13b–d] (b) Dias, A. R.; Dias, P. B.; Diogo, H. P.; Balvao, A. M.; Minas de Piedade, M. E.; Martinho Simões, J. A. *Organometallics* **1987**, *6*, 1427–1432, and references therein. (c) Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1982**, *47*, 205–238. (d) Connor, J. A.; Zarafani-Moattar, M. T.; Bickerton, J.; El Saied, N. L.; Suradi, S.; Carson, E.; Al-Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166–1174, and references therein.

[14] For example, we measure $\Delta H_{soln}(Y(TTB)_2) = 3.5\ (8)$ kcal/mol and $\Delta H_{soln}(TTB) = 2.4\ (2)$ kcal/mol.

[15] Brewer, L. In *Systematics and Properties of the Lanthanides*; Sinha, S. P., Ed.; Reidel: Dordrecht, 1983; pp 17–69.

Reactivity of the Tungsten Carbyne $W(\equiv CCH_3)Cl(PMe_3)_4$: Double Carbonylation, Carbyne–Alkyne Complexes, and Stoichiometric Acetylene Metathesis

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The coupling of carbyne or alkylidyne ligands with unsaturated organic molecules is a fundamental reaction which provides an interesting route to the formation of new carbon–carbon bonds. Coupling of carbyne and carbonyl ligands to form η^1- or η^2-ketenyl complexes has been explored since the initial discovery by Kreissl in 1976[2] and is the subject of a comprehensive recent review.[3] Some high-valent alkylidyne complexes are very active for catalytic acetylene metathesis.[4] We report here the first example of a reaction that couples a carbyne ligand with two molecules of CO,[5] to form an unusual metallacycle, the first carbyne–alkyne complexes,[6] and the first observation of a low-valent ("Fischer-type") carbyne complex undergoing stoichiometric acetylene metathesis.

The tungsten carbyne complex $W(\equiv CCH_3)Cl(PMe_3)_4$ (**1**)[7] reacts with ca. 1 atm of CO to give initially the monosubstituted carbonyl adduct $W(\equiv CCH_3)Cl(CO)(PMe_3)_3$ (**2**) (Scheme I). Complex **2** has been identified by its IR and NMR spectra,[8] which are similar to those of the known $W(\equiv CAr)Cl(CO)(PMe_3)_3$ (Ar = Ph, *p*-tolyl).[9] The monocarbonyl adduct **2** is difficult to isolate, however, because it reacts further with three more molecules of CO to give $\overline{W[OC(PMe_3){=}C(CH_3)C}(O)]Cl(CO)_2(PMe_3)_2$ (**3**), which precipitates from the THF solution (Scheme I). The X-ray crystal structure of **3**[10] (Scheme I) shows a seven-coordinate tungsten(II) center bound in an unusual metallacyclopentene ring via an enolate oxygen and an acyl carbon. The W–O–C–C–C ring is planar to within 3 pm and is well described by the single valence bond structure shown, on the basis of the C–C, C–O, and C–P distances (Scheme I).[11,12]

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[1] Presidential Young Investigator, 1988–1993; Sloan Foundation Fellow, 1989–1991.

[2] Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem.* **1976**, *88*, 649; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632.

[3] Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.*, in press. See also ref 9 and references therein.

[4] Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249–262; *Acc. Chem. Res.* **1986**, *19*, 342.

[5] Addition of two isonitriles to a carbyne has been observed: Baker, P. K.; Barker, G. K.; Gill, D. S.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1321–1331. Gill, D. S.; Baker, P. K.; Green, M.; Paddick, K. E.; Murray, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 986–988.

[6] Carbyne–alkyne complexes are discussed in the following: Mayr, A. *Comments Inorg. Chem.* **1990**, *10*, 227–266. Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227–324. A carbyne–alkyne complex has been suggested in the following: Mayr, A.; Lee, K. S.; Kjelsberg, M. A.; Engen, D. V. *J. Am. Chem. Soc.* **1986**, *108*, 6079–6080. For a related carbyne–alkene complex: Mayr, A.; Dorries, A. M.; McDermott, G. A.; Geib, S. J.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 7775.

[7] Atagi, L. M.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1483–1484.

[8] IR (cm^{-1}, C_6D_6): $\nu_{CO} = 1891$. $^{31}P\{^1H\}$ NMR (d_8-THF): −25.8 (t, 21 Hz, $J_{WP} = 217$ Hz, 1 *P*Me$_3$), −20.2 (d, 21 Hz, $J_{WP} = 275$ Hz, 2 *P*Me$_3$). $^{13}C\{^1H\}$ NMR: 226.8 (dt, $J_{PC} = 45$, 7 Hz, $J_{WC} = 150$ Hz, *C*O), 265.0 (t, $J_{PC} = 7$ Hz, $\equiv CCH_3$).

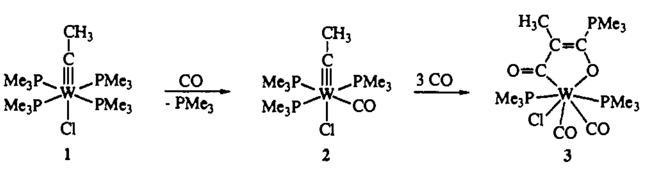
[9] Mayr, A.; Asaro, M. F.; Kjelsberg, M. A.; Lee, K. S.; Van Engen, D. *Organometallics* **1987**, *6*, 432–434.

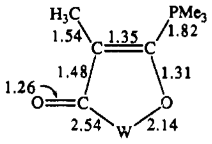
[10] Crystal data for **3**: $WClP_3O_4C_{15}H_{30}\cdot C_4H_8O$, FW = 658.74, monoclinic, $P2_1/c$, $a = 14.945$ (3) Å, $b = 9.259$ (3) Å, $c = 20.226$ (3) Å, $\beta = 102.27$ (10)°, $V = 2735$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 1.60$ g/cm^3, μ(Mo Kα) = 46.1 Å, 3356 unique observed data, $4° < 2\theta < 50°$, $R = 0.035$, $R_w = 0.040$. Data were collected at room temperature on a yellow crystal sealed in a glass capillary under N_2, using a CAD4 diffractometer operating in the θ–2θ scan mode with graphite-monochromated Mo Kα radiation (0.710 73 Å). Empirical absorption corrections were applied. The structures were solved using SHELX direct methods and refined by full matrix least squares.

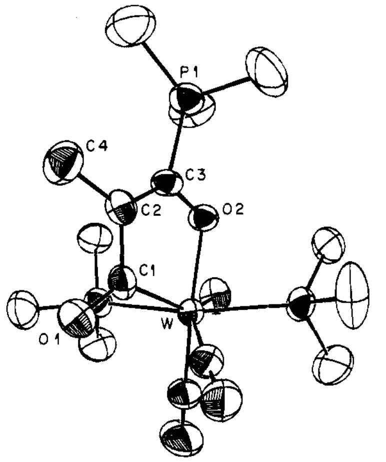
[11] March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1985; p 19.

0002-7863/92/1514-9223$03.00/0

Scheme I



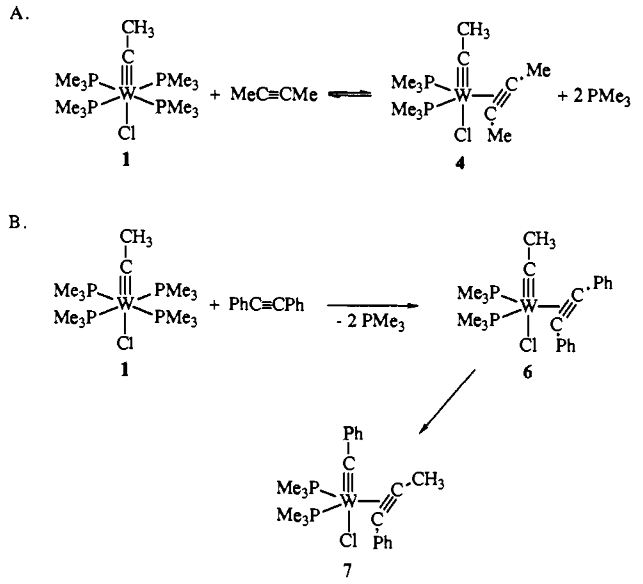




The spectroscopic properties of **3** are consistent with the solid-state structure.[13] IR spectra (CD_2Cl_2) show two carbonyl stretches and an acyl and a C–O single bond stretch (1900, 1809, 1509, 1064 cm^{-1}; confirmed with ^{13}C labeling). The molecule is fluxional on the NMR time scale at 25 °C, but upon cooling to −40 °C the ^{31}P NMR spectra (CD_2Cl_2) show two inequivalent phosphine ligands bound to tungsten (δ −3.3, d, J_{PP} = 154 Hz, J_{WP} = 220 Hz; δ −8.8, d, J_{PP} = 154 Hz, J_{WP} = 195 Hz) and one phosphorus not attached to the metal (δ 16.3, s). The formation of **3** likely proceeds through a ketenyl intermediate formed from the monocarbonyl adduct **2**. The unusual enolate–acyl metallacycle ketenyl can then be formed by both CO insertion[14] and phosphine attack at the electrophilic central ketene carbon,[15] in either order. It is interesting that the closely related $W(\equiv CPh)Cl(CO)_2(PMe_3)_2$ does not undergo these reactions, even on photolysis in neat PMe_3.[9]

The carbyne complex **1** also binds alkenes and alkynes. 2-Butyne reacts with **1** over 3 h at 80 °C in a sealed NMR tube (d_8-THF) to displace 2 equiv of PMe_3 and form an 80% yield of $W(\equiv CMe)Cl(MeC\equiv CMe)(PMe_3)_2$ (**4**; Scheme II).[16] Removal of the volatiles, however, shifts the apparent equilibrium back to **1**, preventing isolation of **4**. Similar reactions are observed with $^tBuC\equiv CH$ (1 day at 24 °C in C_6D_6) and $PhC\equiv CPh$ (4 h at 70 °C in C_7D_8) to form $W(\equiv CMe)Cl(^tBuC\equiv CH)(PMe_3)_2$ (**5**) and $W(\equiv CMe)Cl(PhC\equiv CPh)(PMe_3)_2$ (**6**).[16] Further heating of the diphenylacetylene complex **6** causes the isomerization to the phenylcarbyne–methylphenylacetylene complex, $W(\equiv CPh)Cl(MeC\equiv CPh)(PMe_3)_2$ (**7**, Scheme II), isolated in 63% yield on recrystallization from Et_2O.[16] The *tert*-butylacetylene complex also rearranges on standing to give a number of new products, including the known $W(\equiv C^tBu)Cl(PMe_3)_4$.[17] The carbyne–alkyne complexes have been characterized primarily by NMR: for instance, ^{13}C NMR spectra of **7** show characteristic carbyne (319.8 ppm) and alkyne resonances (175.4, 174.6 ppm). The large downfield shift of the carbyne resonance compared to that for **1** (253.3 ppm) may reflect the competition for π-bonding between the alkyne and carbyne ligands.[6] The phosphine ligands are equivalent in **4** and **6**, reflecting the symmetrical nature of the bound alkyne, but inequivalent in **5** and **7**. The isomerization of **6** to **7** and the conversion of **5** to $W(\equiv C^tBu)Cl(PMe_3)_4$ are single steps along an alkyne metathesis pathway.

Scheme II



Complex **1** also reacts reversibly with $CH_2{=}CHSi(OMe)_3$—the reagent used to form **1** from $WCl_2(PMe_3)_4$[7]—with loss of two phosphines, forming the alkene complex $W[CH_2{=}CHSi(OMe)_3](\equiv CMe)Cl(PMe_3)_2$ (**8**).[18] The vinylalkoxysilane ligand is most likely bound to the tungsten carbyne through both the vinyl group and an ether oxygen (to give an 18e$^-$ count) as $CH_2{=}CHSi(OEt)Me_2$ gives an analogous complex but $CH_2{=}CHSiMe_3$ does not. The three methoxy groups in **8** are equivalent in the NMR at −40 °C in d_8-THF, presumably due to rapid exchange. Further work is in progress to characterize the unusual reactivity of these carbyne complexes.

Acknowledgment. We thank the National Science Foundation and the Exxon Education Foundation for financial support.

Supplementary Material Available: Synthetic procedures and spectral data for **2**–**8** and crystallographic tables for **3** (16 pages); listing of observed and calculated structure factors for **3** (17 pages). Ordering information is given on any current masthead page.

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(12) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier Scientific: New York, 1974; p 397.

(13) ^1H NMR (−40 °C, CD_2Cl_2): 1.21 (d, 9 Hz, 9 H, $WPMe_3$), 1.34 (d, 8 Hz, 9 H, $WPMe_3$), 1.74 (d, 2 Hz, 3 H, $=C(CH_3)$), 1.97 (d, 13 Hz, 9 H, $CPMe_3$). $^{13}C\{^1H\}$ NMR (−50 °C, CD_2Cl_2): δ 257.1, 254.0 (m, $W(CO)_2$), 236.1 (br s, J_{WC} = 136 Hz, $C(O)$), 160.9 (d, J_{PC} = 6 Hz, $WOC(PMe_3)$), 135.1 (d, J_{PC} = 37 Hz, $=C(CH_3)$), 14.2 (d, J_{PC} = 27, $WP(CH_3)_3$), 13.6 (d, J_{PC} = 29, $WP(CH_3)_3$), 9.3 (d, J_{PC} = 53, $CP(CH_3)_3$), 9.2 (s, $=C(CH_3)$). Anal. Calcd for $WClP_3O_4C_{15}H_{30}\cdot 0.7C_4H_8O$: C, 34.09; H, 5.72; O, 12.00. Found: C, 33.78; H, 5.56; O, 12.41.

(14) Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Angew. Chem.* **1978**, *90*, 909; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 859. Eberl, K.; Uedelhoven, W.; Wolfgruber, M.; Kreissl, F. R. *Chem. Ber.* **1982**, *115*, 504. Sieber, W.; Wolfgruber, M.; Neugebauer, D.; Orama, O.; Kreissl, F. R. *Z. Naturforsch.* **1983**, *38b*, 67.

(15) Phosphine attack at phosphinoketenes and arsinoketenes to form metallacycles: Kreissl, F. R.; Sieber, W.; Wolfgruber, M. *J. Organomet. Chem.* **1986**, *317*, 175. Phosphine attack at a coordinated vinylidene: List, A. K.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4855; *Organometallics* **1989**, *8*, 2010.

(16) Selected NMR data for **4** (d_8-THF): ^1H 2.67 (t, 6 Hz, 3 H, $W\equiv CCH_3$), 2.52 (s, 6 H, $MeC\equiv CMe$), 1.65 (t, 4 Hz, 18 H, 2 PMe_3); $^{31}P\{^1H\}$ 9.3 (s, J_{WP} = 191); $^{13}C\{^1H\}$ 321.2 (t, J_{PC} = 19, $W\equiv CMe$), 167.7 (d, J_{PC} = 15, $MeC\equiv CMe$). For **5** (C_6D_6): ^1H 9.42 (m, 1 H, $HC\equiv C^tBu$), 2.77 (t, 6 Hz, 3 H, $W\equiv CCH_3$), 1.38 (s, 9 H, $HC\equiv CCMe_3$), 1.64 (d, 9 Hz, 9 H, PMe_3), 1.44 (d, 8 Hz, 9 H, PMe_3); $^{31}P\{^1H\}$ 8.1 (d, J_{PP} = 84, J_{WP} = 191), −2.9 (d, J_{PP} = 84, J_{WP} = 192). For **6** (C_6D_6): ^1H 2.91 (t, 6 Hz, 3 H, $W\equiv CCH_3$), 1.40 (t, 5 Hz, 18 H, 2 PMe_3), 6.8–7.3 (m, 10 H, $PhC\equiv CPh$); $^{31}P\{^1H\}$ 3.3 (s, J_{WP} = 195). For **7** (C_6D_6): ^1H 1.52, 1.39 (d, 9 Hz, 18 H, 2 PMe_3), 2.57 (t, 1 Hz, 3 H, $MeC\equiv CPh$); $^{31}P\{^1H\}$ 3.4 (d, 93 Hz, J_{WP} = 189), 5.4 (d, 93 Hz, J_{WP} = 187); ^{13}C 319.8 (t, 18 Hz, $W\equiv CPh$), 175.4 (dd, 7, 21 Hz, $MeC\equiv CPh$), 174.6 (m, $MeC\equiv CPh$).

(17) Identified by comparison of ^1H, ^{31}P, and ^{13}C NMR spectra with those in the following: Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322–6329.

(18) Selected NMR data for **8** (d_8-THF): ^1H 3.36 (s, $Si(OMe)_3$), 1.99 (t, 6 Hz, 3 H, $\equiv CCH_3$), 1.25, 0.84, 0.62 (3 br s, 1 H each, $CH_aH_b{=}CH_cSi$); $^{31}P\{^1H\}$ 4.4 (d, 120 Hz, J_{WP} = 236), −7.2 (d, 120 Hz, J_{WP} = 236); $^{13}C\{^1H\}$ (C_6D_6) 277.0 (t, 19, $W\equiv CCH_3$).