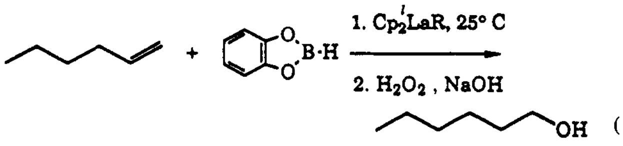
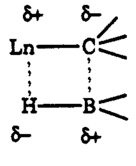
As monitored by NMR, Cp'_2LnR ($Cp' = \eta^5 - Me_5C_5$; Ln = La, Sm; R = H, $CH(SiMe_3)_2$),[4b] $Me_2SiCp''_2LnR$ ($Cp'' = \eta^5$-Me_4C_5; Ln = Sm; R = $CH(SiMe_3)_2$),[5b] and $Cp'_2Sm(THF)$[9] complexes catalyze the room temperature hydroboration of a variety of dry, degassed olefins (25–100-fold stoichiometric excess) with catecholborane at efficient rates (e.g., Cp'_2LaR: $N_t \approx 200$ h^{-1} for 1-hexene, eq 1; $\approx$50 h^{-1} for cyclohexene; $\approx$10 h^{-1} for 1-methcyclohexene).[10,11] As deduced from these and preparative scale experiments (Table I)[12] the reaction encompasses a significant range of olefinic substrates, including terminal (entries 1 and 2), terminal or internal disubstituted (entry 3 and entries 4–6, respectively), and trisubstituted (entry 7 and 8). No reaction is observed for tetrasubstituted 2,3-dimethyl-2-butene at 25 °C. All of these organolanthanide-catalyzed transformations exhibit high regioselectivity (>98% by NMR) with negligible concomitant substrate hydrogenation. Labeling studies with catecholborane-d_1 show that entries 1, 2, 4, and 5 proceed with exclusive (by NMR) delivery of the deuteron to the C2 position (β to B). Both substrate hydrogenation and D label scrambling (presumably via reversible olefin insertion–extrusion) are undesirable accompanying features of many Rh(I)-catalyzed hydroborations.[2,3b,c] The present regiochemistries are exclusively anti-Markovnikov, which for entry 2 contrasts the general pattern observed for the Rh(I)-catalyzed hydroboration of styrenes.[2b–d,3a]



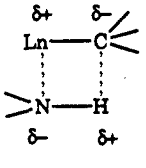
(1)

Regarding mechanistic details, the substrate dependence of rates (for constant Ln complex) follows the ordering terminal ≥ terminal disubstituted > internal disubstituted > trisubstituted, likely reflecting steric demands at the metal center. In accord with this and paralleling a number of other organolanthanide-catalyzed transformations,[4,5b,c,6] both larger metal ions ($N_t(La) \approx 10\ N_t(Sm)$) and more open ancillary ligation ($N_t(Me_2SiCp''_2Ln) \approx 4\ N_t(Cp'_2Ln)$) increase the rate of hydroboration. In common with other organolanthanide-mediated processes, R = H and = $CH(SiMe_3)_2$-based catalysts exhibit indistinguishable turnover frequencies. For the latter substituent, NMR reveals that catalytic turnover is preceded by elimination of $(catechol)BCH(SiMe_3)_2$.[13] This result contrasts other organolanthanide-catalyzed catalytic processes (e.g., hydroamination[6]) in which the Ln–C moieties instead undergo facile protonolysis (e.g., eliminating $CH_2(SiMe_3)_2$). That conveniently prepared $Cp'_2Sm(THF)$ is an efficient precatalyst argues that binuclear substrate C–H activation,[14] to yield Sm(III) hydrocarbyls and hydrides, provides access to the catalytic manifold, as found previously for organosamarium-catalyzed hydroamination.[6c]

The present results can be accommodated by tentative Scheme I, in which Ln–H[15] → Ln–alkyl and B–H + Ln–alkyl → B–alkyl + Ln–H are key transformations. The former (ii) is typically rapid, exothermic,[4,5b,c,8,14] and well-documented in other organolanthanide catalytic sequences. Its importance moreover suggests that hydroboration may be subject to the stereocontrol, functional group tolerance, and follow-up chemistry operative in other Ln–C bond-forming reactions.[4–6] Transpositions (i) and (iii)[16] are estimated[17] to be slightly exothermic (~ –3 kcal/mol) and can be understood vis-à-vis contrasting hydroamination chemistry[6] on the basis of bond polarity arguments (A vs B).



A



B

In summary, these results show that facile catalytic olefin hydroboration can be mediated by organolanthanides and via rather unconventional pathways. Further investigation of this and related catalytic reactions is continuing.

Acknowledgment. We thank N.S.F. (Grant CHE9104112) for generous support of this research. K.N.H. thanks NATO/SERC for a postdoctoral fellowship.

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[10] Uncatalyzed hydroborations using catecholborane typically require temperatures in excess of 100 °C: Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249–5253.

[11] Typical NMR-scale reaction: Under inert atmosphere, a 5-mm NMR tube with a J. Young valve was charged with 0.60 mmol of olefin, 1.2 mmol of catecholborane, 0.30 mL of C_6D_6, and 10 μmol of catalyst. Progress of the hydroboration was monitored via the olefinic ^1H resonances. The alkylborane ester product was identified by ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ spectra.

[12] Typical preparative-scale reaction: Under inert atmosphere, 6.0 mmol of olefin, 20 mmol of catecholborane, and 0.1 mmoL $Cp'_2Sm(THF)$ were stirred in 1.0 mL of benzene at 20 °C. Upon addition of the catecholborane, the reaction solution gradually changed from the characteristic purple of the Sm(II) complex to dark orange-red. Oxidative workup after 14 h with $NaOH/H_2O_2$,[1] followed by diethyl ether extraction, drying, and concentration afforded the product alcohol.

[13] Identified by ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ NMR, and mass spectroscopy.

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[15] (a) We cannot exclude the possibility that the Lewis acidic hydride is present as a hydroborate complex[15b] (e.g., $Cp'_2Ln(\mu\text{-}H)_2B(catechol)$). Efforts to isolate such a complex have so far been unsuccessful. In the absence of olefin, the organolanthanides form complex mixtures of insoluble products (consistent with known catecholborane–metal hydride chemistry).[15c,d] (b) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263–293. (c) Manning, D.; Nöth, H. *J. Organomet. Chem.* **1984**, *275*, 169–171. (d) Manning, D.; Nöth, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1689–1692.

[16] Analogous transpositions: (a) Rh–Me + thexylborane → Rh–H + thexylmethylborane: Baker, R. T.; Ovenall, D. W.; Harlow, R. L.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *Organometallics* **1990**, *9*, 3028–3030. (b) Zr–C(H)═C(H)R + *B*-chlorocatecholborane → Zr–Cl + alkenylcatecholborane: Cole, T. E.; Quintanilla, R.; Rodewald, S. *Organometallics* **1991**, *10*, 3777–3781.

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Organo-f-Element Bonding Energetics. Large Magnitudes of Metal–Arene Bond Enthalpies in Zero-Valent Lanthanide Sandwich Complexes

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The traditional description of metal–ligand bonding in organolanthanides[1] has been one of largely electrostatic interactions necessarily involving metals in relatively high formal oxidation states coordinated to anionic hydrocarbyl/polyene ligands.[1,2]

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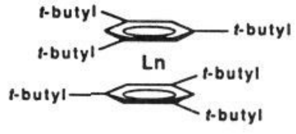
[1] (a) Schumann, H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I., Eds.; D. Reidel: Dordrecht, Holland, 1985; Chapter 1. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131–177. (c) Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Chapter 50. (d) Forsberg, J. H.; Moeller, T. In *Gmelin Handbook of Inorganic Chemistry, Sc, Y, La-Lu Rare Earth Elements, Part D6*; Moeller, T., Krüerke, U., Schleitzer-Rust, E., Eds.; Springer-Verlag: Berlin, 1983; pp 137–303. (e) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21.

Table I. Metal–Ligand Bond Disruption Enthalpies for Zero-Valent Lanthanide and Group 6 Arene Sandwich Complexes (TTB = η^6-1,3,5-t-$Bu_3C_6H_3$)

complex	$\Delta H_{rxn(1)}$ $Ln(TTB)_2$, kcal/mol	ΔH°_f $LnI_{3(c)}$, kcal/mol	ΔH°_{sub} Ln, kcal/mol	D(Ln-TTB), kcal/mol
$Y(TTB)_2$	−116 (3)^a	−153.2 (6)^b	101.5 (5)^c	72 (2)^a
$Gd(TTB)_2$	−108 (3)^a	−143.2 (9)^b	95.0 (5)^c	68 (2)^a
$Dy(TTB)_2$	−128 (2)^a	−147 (2)^b	69.4 (1)^c	47 (2)^a
$Ho(TTB)_2$	−111 (2)^a	−146 (1)^b	71.9 (2)^c	56 (2)^a
$Er(TTB)_2$	−115 (3)^a	−148 (1)^b	75.8 (1)^c	57 (2)^a
$Cr(C_6H_6)_2$				39.4 (1)^d
$Cr(PhEt)_2$				37.5 (1)^d
$Cr(mesitylene)_2$				36.0 (1)^d
$Mo(C_6H_6)_2$				59.0 (1)^d
$W(PhMe)_2$				72.6 (1)^d

[a] Numbers in parentheses are 95% confidence limits. Temperature of measurement, 25 °C. [b] Data of ref 10. [c] Data of ref 11. [d] D(M–arene) data of ref 7d.

Chemical and thermochemical evidence suggests that the metal–ligand bonding in the few known simple lanthanide complexes with neutral olefin,[3] alkyne,[4] and arene[5] ligands is rather weak. In marked contradiction to this picture are recently synthesized, formally zero-valent lanthanide bis(arene) sandwich complexes of the formula $Ln(TTB)_2$ (TTB = η^6-1,3,5-t-$Bu_3C_6H_3$), some of which exhibit impressive thermal stability (sublimable at 100 °C).[6]



$Ln(TTB)_2$

This thermal stability as well as spectroscopic/magnetic evidence suggesting both zero-valent metal character and covalency in metal–ligand bonding[6b] raises intriguing questions about the magnitudes of the metal–arene bond strengths, especially vis-à-vis the more traditional transition element sandwich systems.[7] We communicate here the first thermochemical information on these lanthanide arene complexes which indicates that the metal–arene bonds are very strong.

Iodinolytic batch tritrational calorimetry was carried out in toluene solution using the anaerobic isoperibol instrumentation and procedures described previously.[8] Parallel NMR titrations verified the rapidity and reaction stoichiometry of eq 1.[9] These results are combined with tabulated LnI_3 heat of formation,[10] Ln° heat of sublimation,[11] and I_2 heat of solution[12] data in the ther-

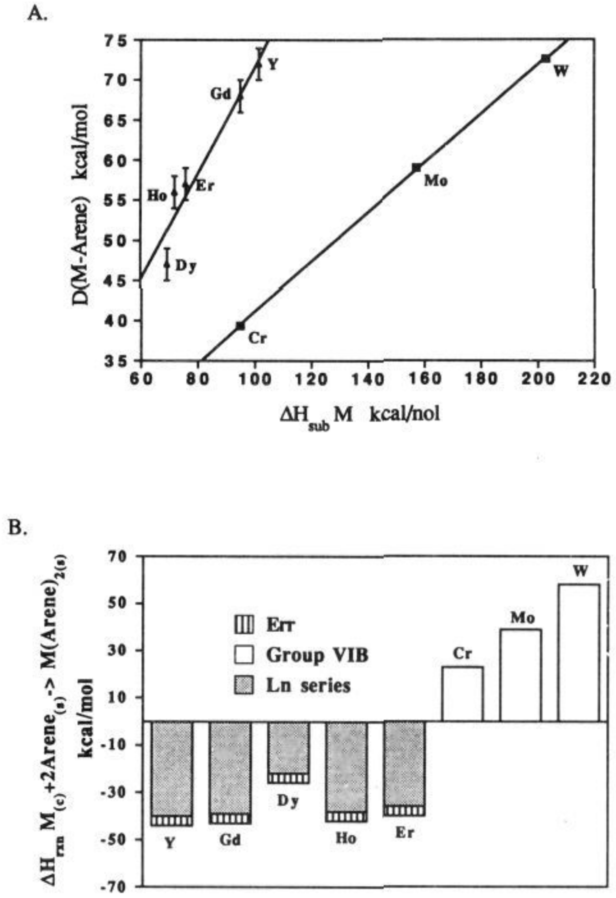


Figure 1. (A) Least-squares plots of metal–arene bond enthalpy values for zero-valent lanthanide (arene = η^6-1,3,5-t-$Bu_3C_6H_3$) and group 6 (arene = η^6-benzene, toluene, or ethylbenzene) arene sandwich complexes versus the standard heats of sublimation of the corresponding bulk metals. (B) Graphical depiction of the calculated formation enthalpies in toluene solution of zero-valent lanthanide (arene = η^6-1,3,5-t-$Bu_3C_6H_3$) and group 6 (arene = benzene, toluene, or ethylbenzene) arene sandwich complexes from the corresponding arene ligands and bulk metals.

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(9) Titrations were carried out in serum-capped NMR tubes by successive microsyringe injections of a stock I_2 solution in C_6D_6 into a $Ln(TTB)_2$ solution of known concentration, followed by vigorous agitation. The $Ln(TTB)_2$ color disappeared at $I_2/Ln = 1.5$, LnI_3 precipitation was complete, and only free TTB signals (correct integration versus an adamantane internal standard) were visible. A preparative scale reaction using $Y(TTB)_2$ yielded insoluble YI_3 after filtration, washing, and drying in vacuo. The powder X-ray diffraction pattern of this material was identical to that of an authentic YI_3 sample.

(10) (a) $\Delta H^\circ_f(YI_3)$: Xiang-Yu, W.; Zhu, J. T.; Goudiakas, J.; Fuger, J. *J. Chem. Thermodyn.* **1988**, *20*, 1995–1202. (b) $\Delta H^\circ_f(DyI_3)$: Morss, L. R.; Spence, T. G. *Z. Anorg. Allg. Chem.*. In press. (c) ΔH°_f data for the other LnI_3's were calculated from the corresponding ΔH_{soln} values of the metals (Gd,[10d] Ho,[10e] Er[10f]), $\Delta H^\circ_f(HI_{(s)})$,[10g] and ΔH_{soln} values of the corresponding LnI_3's,[10h] using methods described elsewhere.[10a,b] (d) Spedding, F. H.; Flynn, J. P. *J. Am. Chem. Soc.* **1954**, *76*, 1474–1477. (e) Bettonville, S.; Goudiakas, J.; Fuger, J. *J. Chem. Thermodyn.* **1987**, *19*, 595–604. (f) Fuger, J.; Morss, L. R.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1980**, 1076–1078. (g) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Harlow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2. (h) Bommer, H.; Hohmann, E. *Z. Anorg. Allg. Chem.* **1941**, *248*, 383–396.

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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 $D(Ln\text{-}TTB)$ 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 $\Delta H_{sub}(Ln)$ 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.

Acknowledgment. We thank N.S.F. (T.J.M., W.A.K., Grant CHE9104112) and B.P. (F.G.N.C., D.M.A., D.J.D.) for support of this research and the Northwestern University Materials Research Center (N.S.F. Grant DMR 8821571) for access to the X-ray Diffraction Facility. We thank Dr. J. Carsella for assistance with the diffraction measurements. We also thank Dr. L. R. Morss for a preprint of ref 10b and for helpful discussions about ΔH°_f LnI_3 data.

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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.

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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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(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 PMe_3), −20.2 (d, 21 Hz, $J_{WP} = 275$ Hz, 2 PMe_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, $\equiv CCH_3$).

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(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 (0.71073 Å). Empirical absorption corrections were applied. The structures were solved using SHELX direct methods and refined by full matrix least squares.

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