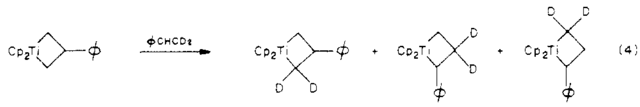
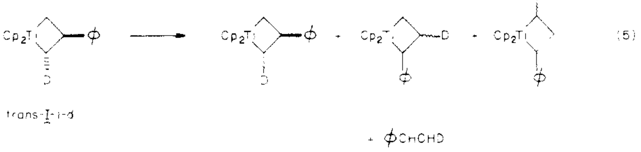


isomerization can occur via carbene or olefin rotation in the metal carbene–olefin complex. High rotation barrier of the carbene rule out the first.[13] To address the olefin rotation possibility, we employed stereospecifically labeled I, since rotation of olefin should define the relative stereochemistry of the α-isomer to be either *trans*-II-*3*-d_1 or *cis*-II-*4*-d_1. Isomerization of *trans*-I-*2*-d_1 in toluene without added styrene, however, gives all possible stereoisomers of II (eq 5). Equal amounts of *cis*- and *trans*-II-*4*-d_1 are



present as are the scrambled β-isomers I-*2*-d_1 and styrene-d_1. We therefore rule out olefin rotation as a major isomerization pathway. From the labeling experiments, we conclude that isomerization of I is due to readdition of olefin to the titanium methylene species (Scheme I).

The intermolecular process is further supported by the following observations. A solution of I-*2,2*-d_2 is allowed to equilibrate at room temperature for 1 h before hydrolysis with anhydrous hydrogen chloride. The organic products are analyzed by GC/MS. Isopropylbenzene is mostly d_2 as expected from unreacted I-*2,2*-d_2. The *n*-propylbenzene, from hydrolysis of II, contained molecules containing from d_0 to d_5 deuteria. The ratio of d_0:d_2:d_4 *n*-propylbenzene is approximately 1:2.5:1.1, or that approaching a statistical olefin exchange[14] (Scheme II). The presence of odd-numbered deuterium atoms in the *n*-propylbenzenes is rationalized in terms of reactions involving titanium hydrides or deuterides that are generated from the decomposition of I.[15]

In contrast to the rearrangement of platinacyclobutanes where a concerted mechanism is suggested, titanacyclobutane isomerizations proceed through a metal–carbene intermediate. This result provides an important step for olefin metathesis in the form of olefin exchange reaction. If the α-isomer could then ring-open to give a substituted metal alkyidene[16] such as $Cp_2Ti{=}CHPh$, a complete metathesis system would then be generated.

Acknowledgment. We acknowledge the financial support of the National Science Foundation. The many helpful discussions and aid of J. Bosco Lee and the technical aid by the Southern California High Field NMR Facility supported by the NSF are gratefully acknowledged.

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[13] Schrock has estimated the ΔG^{*} for the rotation of tantalum alkylidene to be 25 kcal mol^{-1}. Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. The calculated torsional barrier for $Cp_2Ti{=}CH_2$ is 52 kcal mol^{-1}. Frand, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1983**, *2*, 815.

[14] In the presence of a large excess of a 1:1 mixture of styrene-d_0 and -d_2, the kinetic ratio of *n*-propylbenzene d_4:d_2:d_0 should be 1:2.6:1.6. However, under the reaction conditions with no added styrene, both the styrene-d_2/d_0 and the carbene-d_2/d_0 are controlled by the isotope effect and result in a predicted kinetic ratio of 1.6:(1 + 2.56):1.6 or 1:2.2:1. Since multiple exchanges occur, neither of these situations apply directly.

[15] Other decomposition products, ethylbenzene, styrene, and α-methylstyrene, were also detected in significat amounts and showed deuterium scrambling.

[16] Substituted titanium alkylidene species have been observed and isolated. Gilliom, L. R.; Grubbs, R. H., manuscript in preparation.

5f^3 vs. 4f^3. Routes to and Properties of Highly Reactive Neodymium(III) Hydrocarbyl and Hydride Complexes[†]

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Summary: The reaction of $Cp'_2NdCl_2^-Li(ether)_2^+$ ($Cp' = \eta^5\text{-}(CH_3)_5C_5$) with $LiCH[Si(CH_3)_3]_2$ yields the early lanthanide alkyl $Cp'_2NdCH[Si(CH_3)_3]_2$ (**1**). The molecular structure of this complex features an unusually short Nd–methyl contact. Reaction of **1** with hydrogen yields the highly reactive hydride $(Cp'_2NdH)_2$ (**3**). At 25 °C, 1-atm gas pressure, **3** polymerizes ethylene with $N_t > 80\,000$ min^{-1} and hydrogenates 1-hexene with $N_t = 77\,000$ h^{-1}. Cyclohexene is hydrogenated with $N_t = 8300$ h^{-1}. Kinetic measurements indicate that Nd–C hydrogenolysis is rate limiting for 1-hexene and that hydride + olefin addition is rate limiting for cyclohexene.

Despite the recent burgeoning of organoactinide[1] and organolanthanide[1a,2] chemistries, few meaningful comparisons exist between isoelectronic, isoleptic 4f^n and 5f^n systems. A potentially informative comparison to known $Cp'_2UR/(Cp'_2UH)_n$ chemistry[3] ($Cp' = \eta^5\text{-}(CH_3)_5C_5$) would require the corresponding, unknown Nd(III) analogues. Approaches to *ether- and halide-free* compounds of this type are circuitous for later lanthanides[1a,2b,4] and undeveloped for early (La–Nd) lanthanides.[2] We report here that bulky[3,5] hydrocarbyl groups offer a facile *entrée* into such systems, the unusual molecular structure of a $Cp_2'Nd^{III}$ alkyl, and preliminary chemical/mechanistic observations portending very high catalytic activity.

The reaction of $Cp'_2NdCl_2^-Li(ether)_2^+$[6] with [bis(trimethylsilyl)methyl]lithium proceeds according to eq 1 to give hydrocarbyl 1 in 81% isolated yield after recrystal-

$$Cp'_2NdCl_2^-Li(ether)_2^+ + LiCH[Si(CH_3)_3]_2 \xrightarrow[15\text{ h}]{\text{toluene, 0 °C}} \underset{\textbf{1}\text{, blue-green crystals}}{Cp'_2NdCH[Si(CH_3)_3]_2} + 2LiCl + 2\,ether \quad (1)$$

lization from pentane (−30 °C). Complex 1 was characterized by elemental analysis,[7a] infrared spectra,[7b] iso-

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[†] This contribution is dedicated to Earl Muetterties, an outstanding scientist and a friend.

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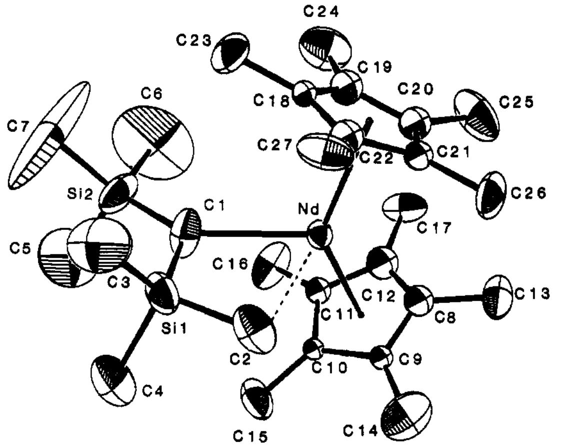

Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms of $Nd[(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$, **1**, with one $(CH_3)_5C_5$ rotamer shown. All atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of the electron density. Individual bond lengths (Å) and angles (deg) of interest include the following $Nd-C_1 = 2.517$ (7); $Nd-C_2 = 2.895$ (7); $C_1-Si_1 = 1.813$ (8); $C_1-Si_2 = 1.814$ (8); $Si_1-C_2 = 1.890$ (9); $Si_1-C_3 = 1.849$ (10); $Si_1-C_4 = 1.849$ (10); $Si_2-C_5 = 1.847$ (13); $Si_2-C_6 = 1.812$ (21); $Si_2-C_7 = 1.891$ (14); average Nd–C(ring) = 2.76 (1, 3, 8, 20);[12] $Nd-C_1-Si_1 = 98.44$ (31); $Nd-C_1-Si_2 = 140.15$ (43); $Si_1-C_1-Si_2 = 121.27$ (44); $Nd-C_2-Si_1 = 84.84$ (27), ring center-of-gravity–Nd–ring center-of-gravity = 134.4. For the two pairs of Cp′ rings, internal metrical parameters are as follows: average C–C = 1.42 (2, 3, 11, 20);[12] average $C-CH_3$ 1.52 (2, 4, 13, 20).[12]

tropically shifted (but readily interpretable) ^1H and ^{13}C NMR spectra,[8] and X-ray diffraction (vide infra). From room temperature to −90 °C, the 270-MHz proton spectra exhibit magnetic inequivalence of the Cp′ rings but magnetic equivalence of the silylmethyl groups.

Single crystals of **1** from pentane are, at −100 °C, monoclinic of space group $P2_1/n$ with $a = 11.045$ (9) Å, $b = 23.554$ (7) Å, $c = 11.648$ (9) Å, $\beta = 103.10$ (6),[9] $Z = 4$, $\mu_a(\text{Mo K}\bar{\alpha}) = 18.6\ \text{cm}^{-1}$, and $d_{calc} = 1.294\ \text{g cm}^{-3}$. Three-dimensional data were collected (5721 independent reflections having $2\theta_{\text{MoK}\bar{\alpha}} < 52°$) on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo radiation and, because of the sizeable mosaic spread, $\omega-2\theta$ scans (ω scan width = $(1.2 + 0.35 \tan \theta)°$). All calculations were performed on a VAX 11/730 computer with Enraf-Nonius SDP software and local programs. The structure was solved by using Patterson and direct methods techniques.[9] The precision of the structure determination was adversely affected by a positional disorder in the Cp′ rings, which could be treated satisfactorily with a model giving 0.5 occupancy to each of two rotamers.[9a] The Cp′ C_5 core atoms were refined isotropically, while all other non-hydrogen atms were refined anisotropically. Structural parameters were refined to convergence [R(unweighted), based on F) = 0.078] for 4287 independent, absorption-corrected reflections having $I > 3\sigma(I)$. The derived metrical parameters are in excellent agreement with more precise results (including approximate H atom locations) for the *ordered* analogue $(CH_3)_2Si[(CH_3)_4C_5]_2NdCH[SiCH_3)_3]_2$ (**2**).[10]

The Cp'_2 ligation in **1** (Figure 1) is unexceptional for 4f/5f $Cp'_2MX/Cp'_2M(X)Y$ complexes.[1,2,6,11,12] However, the Nd–hydrocarbyl fragment is unusual in two respects. Atoms Nd, C_1, Si_1, and Si_2 are coplanar to within 0.02 (1) Å (0.04 (1) Å in **2**),[10b] and a close metal–methyl interaction is evidenced by a $Nd-C_2$ distance only 0.38 (1) Å (15%) longer than the $Nd-C_1$ σ bond distance (0.36 (1) Å longer in **2**). While this interaction does not induce a *statistically* significant lengthening of SiC_2 in **1** (1.890 (9) Å vs. 1.855 (13) Å (average)), it does in **2**[10] (1.928 (8) vs. 1.870 (9) Å (average)). There is no evidence for a CH⋯M interaction[13] in the infrared spectrum of **1**, and $^1J_{^{13}C-H} = 124.5$ Hz (average) is unexceptional for $Si(CH_3)_3$ groups. Taken together, the spectroscopic and structural data[10b] imply an early lanthanide example of an electrophilic, partially bridging interaction that is significantly metal–carbon(methyl) in character.[14] Interestingly, this interaction, the lengthening of $Si-C_2$, and the *syn*-periplanar conformation also suggest an incipient but aborted (a Si═C bond would result) structural model for β-methyl elimination.[15] The variable-temperature NMR results for **1** indicate that this distorted geometry does not lie in a deep potential well.

Compound **1** readily undergoes hydrogenolysis (eq 2) to

$$n\mathbf{1} + n/2\mathrm{H}_2\ \text{(1 atm)} \xrightarrow[3\ \mathrm{h}]{0\ ^{\circ}\mathrm{C,\ pentane}} \underset{\mathbf{3},\ \text{light green microcrystals}}{\overset{\text{92\% isolated yield}}{(\mathrm{Cp'_2NdH})_n}} + n\mathrm{CH_2[Si(CH_3)_3]_2} \quad (2)$$

yield poorly soluble hydride **3**, which has been characterized by standard techniques.[16] Ionic radii[14d] and the infrared spectrum, which is superimposable upon that of $(Cp'_2SmH)_2$[17] ($\nu_{Nd-H} = 1135\ \text{cm}^{-1}$; $\nu_{Nd-D} = 810\ \text{cm}^{-1}$), suggest that $n = 2$.

Compound **3** displays *very high* catalytic activity for ethylene polymerization and olefin hydrogenation. Under

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(7) (a) Anal. Calcd. for $C_{27}H_{49}NdSi_2$: C, 56.49; H, 8.60; Nd, 25.12; Si, 9.78; Li, 0.00. Found: C, 56.26; H, 8.79; Nd, 25.13; Si, 9.70; Li, 0.01. (b) Nujol mull (cm^{-1}): 1250 s, 1248 s, 1080 w, 1030 m, 1015 m, 855 vs, 820 s, 755 w.

(8) ^1H NMR (270 MHz, C_6D_6, 20 °C): δ 61.7 (s, 1 H, lw = 75 Hz), 8.87 (s, 15 H, lw = 15 Hz), 8.73 (s, 15 H, lw = 15 Hz), −16.52 (s, 18 H, lw = 30 Hz). ^{13}C NMR (22.63 MHz, toluene-d_8, 30 °C): δ 988.23 (Si_2CH), 282.04 (Cp′-C), 271.32 (Cp′-C), 8.47 ($Si(CH_3)_3$, −12.82 (Cp′-CH_3), −14.51 (Cp′-CH_3). Although line widths are too broad to allow accurate measurement of the methine $^1J_{^{13}C-H}$ in **1**, the value is 90.0 Hz (very small) in the La analogue.[29a]

(9) (a) See supplementary material for details. (b) DIRDIF: Direct methods applied to difference structure factors to strengthen Fourier methods. Buerskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A. J. "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982.

(10) (a) Jeske, G.; Schock, L. E.; Swepston, P. J.; Schumann, H.; Marks, T. J., submitted for publication. (b) While there is no obvious, directed interaction between C_2 hydrogens and Nd in **2**, the C_1–H vector is severely bent toward the metal.[10a]

(11) (a) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271–3278. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 856–859.

(12) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

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(14) (a) Yb(II)[14b] and Lu(III)[4,14c] examples have been recently reported; correcting for differences in ionic radii,[14d] the $Nd-C_2$ contact in **1** is shorter than in ref 14b and comparable to that in ref 14c. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725–3727. (c) Watson, P. L. "First International Conference on the Chemistry and Technology of the Lanthanides and Actinides", Venice, Sept 5–10, 1983 ($(Cp'_2LuCH_3)_2$). (d) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767. (e) The complexes $[Cp_2M(\mu-CH_3]_2$ (M = Y, Yb)[14f] and $Cp_2M(\mu-CH_3)_2Al(CH_3)_2$ (M = Y, Yb)[14g] have fully bridging methyl groups. (f) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61. (g) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton, Trans.* **1979**, 45–54.

(15) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471–6473.

(16) (a) Anal. Calcd for $C_{20}H_{31}Nd$: C, 57.79; H, 7.52; Nd, 34.70. Found: C, 57.66; H, 8.03; Nd, 34.27. (b) ^1H NMR (270 MHz, C_6D_6, 22 °C): δ 1.80 (s, lw = 52 Hz); the hydride signal could not be located. (c) IR (Nujol mull, cm^{-1}): 1250 w, 1135 s, br, 1020 w, 970 w, 795 w.

(17) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403.

scrupulously anaerobic vacuum line conditions in toluene or cyclohexane solution (25 °C, 1-atm pressure), $N_t > 80\,000\ \mathrm{min}^{-1}$ for ethylene polymerization[18] (product $\bar{M}_n = 233\,000–590\,000$, $\bar{M}_w/\bar{M}_n = 1.91–4.50$);[19] even at −78 °C, $N_t > 16\,000\ \mathrm{min}^{-1}$. Such rates are comparable to or exceed those of the most active "homogeneous" ethylene polymerization catalysts known.[4,20] For $(\mathrm{Cp'_2UH})_n$,[3d] $N_t = 144\ \mathrm{min}^{-1}$, while **1** is inactive. At 25 °C, 1-atm pressure, 1-hexene is hydrogenated by **3** with $N_t = 77\,000\ \mathrm{h}^{-1}$ [21] vs. 6400 h^{-1} for $\mathrm{Ir(COD)P(c\text{-}Hex)_3(py)^+PF_6^-}$ (0 °C),[22] 650 h^{-1} for $\mathrm{Rh(PPh_3)_3Cl}$,[22] and 63 000 h^{-1} for $(\mathrm{Cp'_2UH})_n$.[3] Kinetically, hexene hydrogenation is first order in catalyst (0.10–2.50 mM), first order in $P_{\mathrm{H_2}}$ (0.3–1.5 atm), and zero order (over ca. 99% of the reaction) in olefin. These observations can be most simply accommodated by a scheme[23,24] as in eq 3–5 where [olefin] is high, k_2 and K_2 are large (kinetically[15]

$$(\mathrm{Cp'_2NdH})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{Cp'_2NdH} \quad K_1 \tag{3}$$

$$\mathrm{Cp'_2NdH} + \text{olefin} \underset{(k_{-2})}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{4}}{\mathrm{Cp'_2NdR}} \quad K_2 \tag{4}$$

$$\mathrm{Cp'_2NdR} + \mathrm{H_2} \xrightarrow{k_3} \mathrm{Cp'_2NdH} + \text{alkane} \tag{5}$$

and thermodynamically[15,25] reasonable; verified by NMR), and hydrogenolysis (k_3) is rate limiting. Note that classical oxidative addition/reductive elimination sequences[22,26] are inappropriate for Nd(III). At 31% conversion, 4.1% of the olefin is present as 2-hexene, suggesting β-H elimination can occur from **4** (2- or 3-hexyl); under $\mathrm{D_2}$, this 2-hexene is predominantly d_1, the unreacted 1-hexene predominantly d_0, and the hexane predominantly 1,2-d_2.[27] For cyclohexene, $N_t(\max) = 8300\ \mathrm{h}^{-1}$, and the reaction is first order in olefin, $^1/_2$ order in catalyst (0.58–11.6 mM), and zero order in $P_{\mathrm{H_2}}$ (0.55–1.4 atm). Equations 3–5 accommodate this observation if k_2 is now rate limiting (sterically, kinetically, and thermodynamically[25] reasonable; verified by NMR). To our knowledge, these data represent some of the first detailed kinetic/mechanistic observations on early transition[26,28] and f-element[1,2,17] homogeneous hydrogenation catalysis. The efficiency with which eq 4 and 5 can be coupled is particularly remarkable, as is, for both polymerization and hydrogenation, the increase in overall activity over the uranium analogue.

The present results offer new synthetic routes to highly reactive early (and other[29a]) organolanthanides and the first opportunities to acquire comparative 4f/5f mechanistic information. Further studies are in progress and will be reported in due course.[10a,29]

Acknowledgment. We thank Molycorp for support of this research and Prof. R. L. Burwell, Jr., and G. Jeske and H. Lauke for helpful discussions.

Registry No. 1, 93383-00-7; **3**, 93303-98-1; $\mathrm{Cp'_2NdCl_2^-Li(ether)_2^+}$, 78128-14-0; $\mathrm{LiCH[Si(CH_3)_3]_2}$, 41823-71-6; $\mathrm{CH_2[Si(CH_3)_3]_2}$, 2117-28-4; ethylene, 74-85-1; polyethylene, 9002-88-4; 1-hexene, 592-41-6; cyclohexene, 110-83-8.

Supplementary Material Available: Structure report and tables of fractional atomic coordinates and anisotropic thermal parameters as well as bond distances and angles and structure factors (61 pages). Ordering information is given on any current masthead page.

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(18) Measured aliquots of catalyst solution were injected into a rapidly stirred, solvent-filled Morton flask maintained at 1 atm of ethylene. After a measured time interval, polymerization was quenched with methanol, and polyethylene was collected, washed, and dried.

(19) GPC in o-$\mathrm{C_6H_4Cl_2}$. The dependence of molecular weight and polydispersity upon reaction conditions will be discussed elsewhere.[29a] We thank Dr. Mark Delaney (Dow Central Research) for these measurements.

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(29) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J., submitted for publication ($\mathrm{Cp'_2MCH[Si(CH_3)_3]_2}$, M = La, Nd, Sm, Lu). (b) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J., submitted for publication. (c) **Note added in proof.** The new complexes $\mathrm{Cp'_2YCH[Si(CH_3)_3]_2}$ and $(\mathrm{Cp'_2YH})_2$ have been recently reported and appear to have very similar structures: Den Haan, K. H.; Teuben, J. H., NATO Advanced Study Institute "Fundamental and Technological Aspects of Organo-Element Chemistry", Maratea, Italy, Sept 10–21, 1984.

Chemical and Electrochemical Reactivity of Some Unsaturated Hexanuclear Osmium–Gold Clusters[†]

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Summary: The unsaturated clusters $\mathrm{Os_4(CO)_{12}(AuPR_3)_2}$ [$\mathrm{PR_3 = PEt_3}$ (I), $\mathrm{PPh_3}$ (II), $\mathrm{PMePh_2}$ (III)] may be prepared by the thermal decarbonylation of $\mathrm{Os_4(CO)_{13}(AuPR_3)_2}$ [$\mathrm{PR_3 = PEt_3}$ (IV), $\mathrm{PPh_3}$ (V), $\mathrm{PMePh_2}$ (VI)] which have been obtained previously by the reaction of $[\mathrm{Os_4H(CO)_{13}}]^-$ with 2 equiv of $\mathrm{Au(PR_3)Cl}$. The former reaction is reversible, and clusters I, II, and III readily add a range of nucleophiles as well as undergoing facile sequential, electrochemical reductions, to $[\mathrm{Os_4(CO)_{12}(AuPR_3)_2}]^-$ and $[\mathrm{Os_4(CO)_{12}(AuPR_3)_2}]^{2-}$. The existence of the monoanionic species is confirmed by the observation of an ESR spectrum, while X-ray crystallographic studies on III and IV show "open" bicapped butterfly and diedge-bridged tetrahedral metal frameworks, respectively.

Substitution reactions at metal centers in low-valent carbonyl clusters generally proceed via a dissociative

[†] Dedicated to the memory of Earl L. Muetterties.