1.[6] Both compounds are structurally similar and consist of a central tetraosmium core arranged in a tetrahedral geometry with two Pt(COD) groupings capping triangular faces. The M_6 cluster is thus very similar to that of the parent osmium cluster $Os_6(CO)_{18}$.[7]

Complex 1 is electronically saturated and exhibits no unusual distortions. Each osmium atom contains three terminal carbonyl ligands. All six osmium-osmium bonds lie within the range 2.786 (1)-2.868 (1) Å, which is similar to the range of values found in $Os_6(CO)_{18}$ (2.732-2.808 Å) for the central Os_4 grouping.[7] The osmium-platinum distances span a fairly wide range (2.711 (1)-2.975 (1) Å), but none are unusually long or unusually short.[8]

On the other hand, complex 2, which has one less carbonyl ligand than 1, is electron-deficient by the amount of two electrons. The structure of 2 shows that several of its metal-metal bonds are considerably shorter than those in 1. For example, the Os(2)-Os(3) distance in 2 is 2.530 (1) Å. It is over 0.25 Å shorter than the corresponding distance in 1 and is nearly 0.20 Å shorter than the corresponding Os-Os distance observed in $Os_6(CO)_{18}$.[7] It is one of the shortest Os-Os distances ever observed in an osmium cluster complex.[10] Os-Os triple-bond distances range from 2.182 (1) Å[12] to 2.467 (1) Å.[13] Although the Os(2)-Os(3) bond contains a bridging carbonyl ligand, structural characterizations of the few osmium cluster complexes that have been shown to contain bridging carbonyl ligands show that these bridging ligands do not produce a significant shortening of osmium-osmium bonds.[14] In addition, three of the other metal-metal bonds in 2 are also substantially shorter than those in 1. These are Os(1)-Os(4) (2.705 (1) Å in 2 vs 2.832 (1) Å in 1), Pt(1)-Os(3) (2.609 (1) Å in 2 vs 2.741 (1) Å in 1), and Pt(2)-Os(2) (2.614 (1) Å in 2 vs 2.855 (1) Å in 1). It is believed that the shortening of the metal-metal bonds in 2 is a direct consequence of its electronic unsaturation, although differences in the coordination of the COD ligands to the platinum atoms may also affect these and some of the other metal-metal bond distances. The shortness of the Os(2)-Os(3) bond suggests the unsaturation is greatest at this position.

We have found that the reactivity of 2 is also indicative of unsaturation. For example, when 2 was exposed to CO (1 atm/25 °C) in CH_2Cl_2 solvent, it was converted to 1 in 84% yield in 15 min. The thermal decarbonylation of 1 to 2 at 97 °C in heptane solvent is fraught with much decomposition, but 2 can be obtained in low yield (7%). In contrast, compound 2 was obtained cleanly from 1 when its solutions were exposed to UV radiation at 25 °C in the presence of a nitrogen purge (77% yield after 11 h). We expect that compound 2 will show enhanced reactivity to the addition of a wide range of small molecules. These studies are in progress.

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Supplementary Material Available: Tables of crystal data, positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters for the structural analysis of compounds 1 and 2 (23 pages); listings of structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

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[6] Dark brown crystals of 1 were grown from solution in a CH_2Cl_2/hexane solvent mixture by slow evaporation of solvent at 10 °C. Crystal data for 1: space group $P\bar{1}$, $a = 11.217$ (2) Å, $b = 17.295$ (3) Å, $c = 8.866$ (2) Å, $\alpha = 92.88$ (2)°, $\beta = 105.82$ (2)°, $\gamma = 104.23$ (2)°, $Z = 2$. Dark brown crystals of 2 were grown from solution in a CH_2Cl_2/hexane solvent mixture by slow evaporation of solvent at 25 °C. Crystal data for 2: space group $P2_1/c$, $a = 8.622$ (2) Å, $b = 21.917$ (5) Å, $c = 16.767$ (3) Å, $\beta = 95.61$ (2)°, $Z = 4$. Both structures were solved by a combination of direct methods and difference Fourier techniques. Compound 1 was refined with 3084 reflections to the final R values $R = 0.038$ and $R_W = 0.043$. Compound 2 was refined with 2698 reflections to the final R values $R = 0.033$ and $R_W = 0.034$. Diffraction data were collected on a Rigaku AFC6S diffractometer by using Mo Kα radiation. Calculations were performed on a MICROVAX II computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Data were corrected for absorption.

[7] Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802.

[8] A thorough compilation of Os-Pt distances for osmium-platinum carbonyl cluster complexes is given in a very recent review.[9]

[9] Farrugia, L. J. *Adv. Organomet. Chem.*, in press.

[10] A similarly short Os-Os distance, 2.537 (1) Å, was observed in the unsaturated cluster complex $Pt_2Os_6(CO)_{16}(COD)_2$.[11]

[11] Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1395.

[12] Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4850.

[13] (a) Ren, T. Ph.D. Dissertation, Texas A&M University, 1990. (b) Cotton, F. A. Personal communication.

[14] Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Kaner, D. A.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 961.

Reaction of Diethylaluminum Chloride with Diaza-18-crown-6. Synthesis and Molecular Structure of $[(EtAl)_2{\cdot}\text{diaza-18-crown-6}]^{2+}$: A Novel Aza Crown Ether Stabilized Square-Pyramidal Coordination of Aluminum

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Summary: The crystalline complex $[(EtAl)_2{\cdot}\text{diaza-18-crown-6}][EtAlCl_3]_2$ has been prepared and its structure determined by X-ray diffraction. The $[(EtAl)_2{\cdot}\text{diaza-18-crown-6}]^{2+}$ cation contains two five-coordinate aluminum atoms, both residing in square-pyramidal environments. The title compound appears to have resulted from an interesting disproportionation of diethylaluminum chloride.

The interactions of aluminum species with oxygen-based ligands represent one of the fundamental cornerstones of organoaluminum chemistry. The last decade has witnessed an impressive body of work in this area. Particularly noteworthy are studies concerning the organoaluminum chemistry of oxygen-based macrocyclic ligands, crown ethers. Seminal studies by Atwood et al.[1,2] demonstrated the unique ability of organoaluminum moieties, upon adduct formation, to greatly distort crown ethers, forcing them to assume unusual exodentate conformations. Re-

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[1] Atwood, J. L.; Hrncir, D. C.; Shakir, R.; Dalton, M. S.; Priester, R. D.; Rogers, R. D. *Organometallics* **1982**, *1*, 1021.

[2] Atwood, J. L.; Hrncir, D. C.; Priester, R. D.; Rogers, R. D. *Organometallics* **1983**, *2*, 985.

0276-7333/91/2310-0036$02.50/0

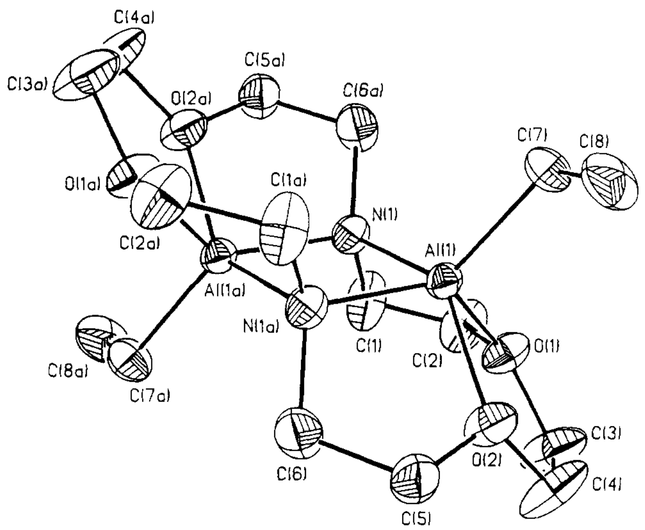

Figure 1. Thermal ellipsoid plot of the [(EtAl)$_2$·diaza-18-crown-6]$^{2+}$ cation showing the atom-labeling scheme. Thermal ellipsoids show 20% probability levels; hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): Al(1)-C(7) = 1.944 (5), Al(1)-O(1) = 1.950 (5), Al(1)-O(2) = 1.959 (5), Al(1)-N(1) = 1.972 (3), Al(1)-N(1a) = 1.963 (4), Al(1)···Al(1a) = 2.902 (3); C(7)-Al(1)-N(1) = 114.5 (2), C(7)-Al(1)-N(1a) = 117.1 (2), C(7)-Al(1)-O(1) = 108.9 (2), C(7)-Al(1)-O(2) = 106.3 (2), O(1)-Al(1)-N(1) = 82.9 (2), O(1)-Al(1)-O(2) = 76.9 (2), N(1)-Al(1)-N(1a) = 85.0 (2), O(2)-Al(1)-N(1a) = 83.3 (2), Al(1)-C(7)-C(8) = 117.2 (5); O(1)-Al(1)-N(1a) = 133.4 (2); N(1)-Al(1)-O(2) = 138.5 (2).

cently this laboratory initiated investigations into the corresponding organoaluminum chemistry of nitrogen-based crown ethers, aza crown ethers. Reactions of organoaluminum species with aza crown ethers containing N-H moieties have been shown to eliminate R-H and result in products possessing extensive Al-N association.[3,4] In an effort to examine the effect of crown ethers containing both oxygen and nitrogen donor atoms on organoaluminum coordination chemistry, the oxygen-nitrogen mixed-donor crown ether 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, diaza-18-crown-6, was allowed to react with diethylaluminum chloride in toluene.[5] The crystalline complex [(EtAl)$_2$·diaza-18-crown-6][EtAlCl$_3$]$_2$ was isolated in high yield. Diaza-18-crown-6 was chosen for this study, as it was recently demonstrated to stabilize a five-coordinate trigonal-bipyramidal organogallium moiety in the [Me$_2$Ga·diaza-18-crown-6][Me$_3$Ga]$_2$ complex.[6] A thermal ellipsoid plot of the [(EtAl)$_2$·diaza-18-crown-6]$^{2+}$ cation is given in Figure 1.

X-ray intensity data were collected on a Nicolet R3m/V diffractometer using an $\omega/2\theta$ scan technique with Mo Kα radiation (λ = 0.71073 Å) at 21 °C. The title compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a = 12.293 (4) Å, b = 11.115 (4) Å, c = 14.154 (5) Å, β = 115.88 (2)°, D_{calcd} = 1.33 g cm^{-3}, and V = 1740 (1) Å^3 for Z = 2. Non-hydrogen atoms were refined with use of anisotropic thermal parameters. Hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculation at idealized positions (d_{C-H} = 0.96 Å). An isotropic group thermal parameter (U_{iso} = 0.174 (8) Å^2) was refined for all hydrogen atoms. The structure was solved by direct methods and refined, on the basis of 1603 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.50 < 2\theta < 45.0°$, with use of SHELXTL.[7] Peaks on the final difference map ranged from −0.19 to 0.29 e Å^{-3}. Refinement converged at R = 0.051 and R_w = 0.069.

The [(EtAl)$_2$·diaza-18-crown-6]$^{2+}$ cation resides about a crystallographic center of symmetry. The aza crown has been greatly distorted, as a planar Al$_2$N$_2$ four-membered ring occupies the central cavity of the cation. The Al-N-Al bond angle is 95.0 (2)°, while the N-Al-N bond angle is 85.0 (2)°. The Al···Al contact of 2.902 (3) Å does not suggest significant metal-metal interaction. Indeed, the general conformation of the aza crown in the cation is surprisingly similar to that observed for [14]aneN$_4$ in [(MeAl)$_2$[14]aneN$_4$][Me$_3$Al]$_2$.[8] The mean Al-N bond distance in the cation of 1.968 (6) Å compares to 1.955 (6) Å for the mean Al-O bond distance. The most striking feature of the cation, however, concerns the coordination of the aluminum atoms. The coordination sphere of each aluminum atom in the cation is composed of two nitrogen and two oxygen atoms of the aza crown in addition to an ethyl group. As the four donor atoms of the crown constitute a basal plane while the ethyl group occupies an apical position, the coordination of both aluminum atoms in the cation may be described as square pyramidal. Indeed, the [(EtAl)$_2$·diaza-18-crown-6]$^{2+}$ cation is noteworthy, as it represents the first report of an organoaluminum-crown ether complex containing two five-coordinate organoaluminum moieties both residing in square-pyramidal geometries. The Al(1)-C(7) bond distance of 1.944 (5) Å compares well with other Al-C bond distances of five-[9] and six-coordinate[10] organoaluminum species.

The organoaluminum-Schiff base compound [EtAl·SALEN][11] provides an informative comparison with the [(EtAl)$_2$·diaza-18-crown-6]$^{2+}$ cation. The elimination of ethyl groups from Et$_3$Al was shown to be a stepwise process in the presence of Schiff bases in this study. The aluminum atom in [EtAl·SALEN] was shown to be five-coordinate, residing in a square pyramidal geometry with the basal plane consisting of two nitrogen and two oxygen atoms of the Schiff base and the ethyl group residing in an apical position. The aluminum atom was shown to be displaced 0.540 Å from the O$_2$N$_2$ basal plane in [EtAl·SALEN], while the aluminum atom in the [(EtAl)$_2$·diaza-18-crown-6]$^{2+}$ cation is displaced 0.732 Å from the O$_2$N$_2$ plane. The Al-C bond distance of 1.966 (7) Å is a bit longer than the distance of 1.944 (5) Å observed for the [(EtAl)$_2$·diaza-18-crown-6]$^{2+}$ cation. The Al-N bond dis-

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(3) Robinson, G. H.; Self, M. F.; Sangokoya, S. A.; Pennington, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 1520.

(4) Sangokoya, S. A.; Moise, F.; Pennington, W. T.; Self, M. F.; Robinson, G. H. *Organometallics* **1989**, *8*, 2584.

(5) Inside the drybox a reaction tube was charged with diaza-18-crown-6 (0.953 mmol) and toluene (20 mL). The mixture was stirred for 10 min until all the crown ether had dissolved. A slight excess of diethylaluminum chloride (6.22 mmol) was added slowly via syringe. The resulting clear solution was capped, removed from the drybox, and heated at 120 °C in an oil bath for 48 h. The reaction tube was vented frequently. Cooling to −4 °C overnight resulted in the formation of clear, rectangular, extremely air-sensitive X-ray-quality crystals in approximately 78% yield (based on diaza-18-crown-6); mp 168 °C. ^{1}H NMR (Bruker 300 MHz, CDCl$_3$): δ −0.180 (q, 8 H, AlCH_2CH$_3$), 1.00 (t, 12 H, AlCH$_2$CH_3), 3.70 (m, 24 H, diaza-18-crown-6).

(6) Lee, B.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1990**, *9*, 1709.

(7) Sheldrick, G. M. SHELXTL, Crystallographic Computing System, Revision 5.1; Nicolet Instruments Division: Madison, WI, 1986.

(8) Robinson, G. H.; Rae, A. D.; Campana, C. F.; Byram, S. K. *Organometallics* **1987**, *6*, 1227.

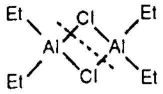
(9) (a) Kai, Y.; Yasuoka, N.; Kasai, N.; Kakudo, M. *J. Chem. Soc. D* **1969**, 575. (b) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779. (c) Goedken, V. L.; Haruko, I.; Ito, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1453. (d) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6852. (e) Sierra, M. L.; De Mel, V. S.; Oliver, J. O. *Organometallics* **1989**, *8*, 2486. (f) Lee, B.; Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1990**, *21*, 99.

(10) (a) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 398. (b) Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 1828.

(11) Dzugan, S. J.; Goedken, V. L. *Inorg. Chem.* **1986**, *25*, 2858.

tances observed in the cation (1.968 (6) Å) are shorter than those reported for [EtAl·SALEN] (2.013 (6) and 2.027 (6) Å), while the Al–O bond distances observed for the cation (1.955 (6) Å) are longer than those reported for the Schiff base complex (1.800 (5) and 1.829 (5) Å).

It is interesting to consider an unusual disproportionation of diethylaluminum chloride wherein $\mathrm{Et_2Al^+}$ and $\mathrm{EtAlCl_3^-}$ contribute to the formation of the title compound. While the symmetric bridge cleavage of dihalo-bridged dimers of alkylaluminum halides (I) is commonplace, the asymmetric bridge cleavage of mixed chloro–alkyl-bridged dimers is much less often encountered. Asymmetric cleavage of the mixed chloro–ethyl-bridged dimer of diethylaluminum chloride (II) would readily result in $\mathrm{Et_2Al^+}$ and $\mathrm{Et_2AlCl_2^-}$. It is reasonable that reaction of $\mathrm{Et_2Al^+}$ with the aza crown could afford the $\mathrm{[(EtAl)_2{\cdot}diaza\text{-}18\text{-}crown\text{-}6]^{2+}}$ cation. Symmetrical cleavage of the mixed chloro–ethyl-bridged dimer of diethylaluminum chloride (III) would result in $\mathrm{Et_3Al}$ and $\mathrm{EtAlCl_2}$. One could envisage the $\mathrm{EtAlCl_3^-}$ anion of $\mathrm{[(EtAl)_2{\cdot}diaza\text{-}18\text{-}crown\text{-}6]^{2+}}$ resulting from reaction of $\mathrm{Et_2AlCl_2^-}$ with $\mathrm{EtAlCl_2}$.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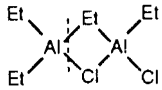
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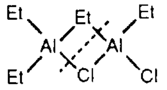
III

There is precedence for aluminum moieties behaving in this manner, as asymmetric bridge cleavage of aluminum–chloro dimers was previously reported by Atwood et al. in the generation of the $\mathrm{Cl_2Al^+}$ cation.[12] Disproportionation of alkylaluminum halides resulting in mixed alkyl–halo-bridged dimers has been observed in this laboratory.[13] Moreover, Atwood et al. reported that the related $\mathrm{Me_2Al^+}$ ion was stabilized by 18-crown-6 in the $\mathrm{[Me_2Al{\cdot}18\text{-}crown\text{-}6]^+}$ cation.[14] Indeed, the same anion that was isolated in our system, $\mathrm{[EtAlCl_3]^-}$, was isolated as the anion of $\mathrm{[Cl_2Al{\cdot}18\text{-}crown\text{-}6]^+}$.[15]

This study indicates that the chemistry of mixed-donor crown ethers differs substantially from that of non-mixed-donor crown ethers. Moreover, the coordination chemistry of aluminum in these systems is quite unpredictable. This study will be used as a bench mark as we continue to explore the organoaluminum chemistry of mixed-donor crown ethers.

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Supplementary Material Available: A summary of data collection and refinement, plots of molecules, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (12 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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[12] (a) Means, N. C.; Means, C. M.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* **1987**, *26*, 1466. (b) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796.

[13] (a) Moise, F.; Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1990**, *21*, 129. (b) Sangokoya, S. A.; Moise, F.; Pennington, W. T.; Self, M. F.; Robinson, G. H. *Organometallics* **1989**, *8*, 2584. (c) Robinson, G. H.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 1453.

[14] Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 485.

[15] Atwood, J. L.; Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom.* **1984**, *2*, 367.

Silylformylation of 1-Hexyne Catalyzed by Rhodium–Cobalt Mixed-Metal Carbonyl Clusters

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Summary: Reactions of hydrosilanes with 1-hexyne catalyzed by $\mathrm{Co_2Rh_2(CO)_{12}}$ and $\mathrm{Rh_4(CO)_{12}}$ at 25 °C and atmospheric pressure–150 psi of carbon monoxide give (*Z*)-1-silyl-2-formyl-1-hexenes (**1**), which are the products of "silylformylation", and/or (*E*)-1-silyl-1-hexenes (**2**). The ratio of silylformylation vs hydrosilylation products depends on the electronic nature of hydrosilane used. Depending on the conditions, the reaction gives 2,4-di-*n*-butyl-3-silylcyclopent-2-en-1-one (**3**) as a major side product, which is a unique carbometalation–cyclization product. The novel Rh–Co mixed-metal complexes $\mathrm{(PhMe_2Si)_2Rh(CO)_{\mathit{n}}Co(CO)_4}$ (n = 2, 3); **6a** and $\mathrm{RhCo(\mathit{n}\text{-}BuC{\equiv}CH)(CO)_5}$ (**7**) are found to be important catalyst species for silylformylation catalyzed by $\mathrm{Co_2Rh_2(CO)_{12}}$. Possible catalytic cycles of silylformylation that can accommodate the observed results are proposed.

The silicon version of hydroformylation of olefins is known as "silylcarbonylation", discovered by Murai et al.,[3] which is promoted by $\mathrm{Co_2(CO)_8}$ to give silyl enol ethers of homologous aldehydes. In Murai's silylcarbonylation, the silicon moiety always attaches to oxygen; viz., any silicon migration to the olefinic bond to form a silicon–carbon bond is not observed at all. As a part of our study on the catalysis of Co–Rh mixed-metal complexes such as $\mathrm{Co_2Rh_2(CO)_{12}}$ and $\mathrm{CoRh(CO)_7}$,[4,5] we have been investigating the reactions of $\mathrm{Co_2Rh_2(CO)_{12}}$ and $\mathrm{CoRh(CO)_7}$ with hydrosilanes in the presence and absence of carbon monoxide and/or substrates to determine the active sites of these Co–Rh mixed-metal catalyst systems by identifying active catalyst species as well as intermediates for catalytic cycles. In order to examine possible synergistic effects in the Co–Rh mixed systems, $\mathrm{Rh_4(CO)_{12}}$ and $\mathrm{Co_2(CO)_8}$ have also been used as references.

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[3] Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837 and references cited therein.

[4] Ojima, I. *Chem. Rev.* **1988**, *88*, 1011 and references cited therein.

[5] Ojima, I.; Okabe, M.; Kato, K.; Kwon, H. B.; Horváth, I. T. *J. Am. Chem. Soc.* **1988**, *110*, 150.