of the chloride bridge with a hydride bridge followed by inversion of hydride (**6-H**$_b$ $\rightleftharpoons$ **6-H**$_c$)—or the formation of a linear hydride bridge—and reformation of the chloride bridge would account for the equivalence of the methylene hydrogens on dppm. The palladium–palladium distance in **6-H**, 3.01 Å, is sufficient to accommodate this process (Pd–H = 1.56 ± 0.04 Å). This not only would lead to the observed equivalence but also provides a mechanism by which hydride and methyl become bonded to the same palladium. In fact, an intermediate consistent with a methyl and a hydride ligand on the same palladium center is observed for the chloride salt of **6-H** during the reductive elimination.[14] The role of the LiCl is not completely understood, but apparently the terminal bonding of chloride is effective in shifting the equilibrium to the complex with both methyl and hydride on one palladium. The hydride and methyl ligands in complexes **6-H**$_b$ and **6-H**$_c$, however, are trans, and an isomerization to a cis complex would be required prior to reductive elimination,[15] probably by dissociation of one phosph. ' of dppm.[16] The observation of two new ^{31}P NMR signals at δ 3 and +16 during the course of the reaction is consistent with h a species.

The reductive elimination re ions of other dinuclear palladium complexes containing hydride a   rganic ligands and the reaction of **6-H** with carbon monoxide a..u other small molecules will be reported in the future.

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(14) ^{1}H NMR (CD$_2$Cl$_2$, -25 °C) δ -0.49 (t, *J* = 4 Hz, 3 H), -10.92 (t, *J* = 11 Hz, 1 H). The coupling between the hydride and the methyl protons could not be resolved.

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A New Type of Carbene Catalyst. Direct Evidence for the Involvement of Coordinated Carbenes in a Cluster-Catalyzed Transalkylation Reaction between Tertiary Amines

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Catalytic transalkylation of tertiary amines is a new and potentially valuable method for the synthesis of unsymmetrical tertiary amines (eq 1, R, R' = alkyl). C–H activations in the

$$NR_3 + NR'_3 \rightleftharpoons NR_2R' + NRR'_2 \qquad (1)$$
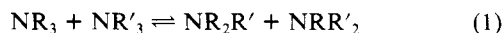
alkyl groups occur in conjunction with the transalkylation, and this has led to the proposal that iminium ion complexes are important intermediates.[1-4] We now wish to report on the preparation and characterization of an unusual amino–carbene cluster complex that is also a very effective catalyst for the transalkylation reaction.

(1) Murahashi, S.-I.; Hirano, T.; Yano, T. *J. Am. Chem. Soc.* **1978**, *100*, 348.

(2) (a) Laine, R. M.; Wilson, R. B., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 361. (b) Shvo, Y.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753.

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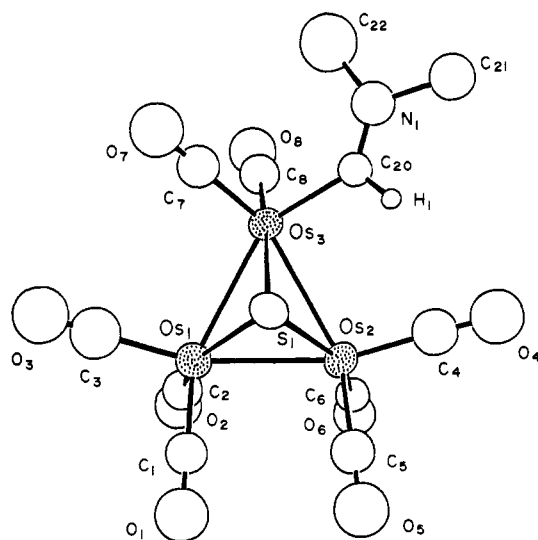
Figure 1. ORTEP drawing of one of the two symmetry independent molecules found in the crystal of Os$_3$(CO)$_8$[C(H)NMe$_2$](μ-H)$_2$(μ_3-S) (**1**).

Under an atmosphere of NMe$_3$ at 125 °C in octane solvent the sulfido cluster Os$_3$(CO)$_9$(μ_3-CO)(μ_3-S)[5] adds one formula equivalent of NMe$_3$ to yield the new compound Os$_3$(CO)$_8$[C(H)NMe$_2$](μ-H)$_2$(μ_3-S) (**1**) (31% yield). Compound **1** has been characterized by IR and ^{1}H NMR spectroscopies and by a single-crystal X-ray diffraction analysis.[6] The compound crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric crystal unit. Both molecules are very similar structurally and an ORTEP drawing of one of these is shown in Figure 1.[7] The molecule consists of a triangular cluster of three osmium atoms bridged by a triply bridging sulfido ligand. The presence of two inequivalent hydride ligands was established by ^{1}H NMR spectroscopy, δ -20.38, -21.18. They were not observed in the crystallographic analysis, but the significant elongation of two of the three metal–metal bonds (e.g., Os(1)–Os(3) = 2.911 (1) Å, and Os(2)–Os(3) = 2.922 (1) Å vs. Os(1)–Os(2) = 2.768 (1) Å) indicates that they are bridging these two bonds. This portion of the molecule is very similar to that of Os$_3$(CO)$_9$(μ_2-H)$_2$(μ_3-S).[8] The most interesting and unusual feature of compound **1** is the presence of a (dimethylamino)carbene ligand, C(H)NMe$_2$. Although not unprecedented, secondary aminocarbene ligands are not commonly occurring.[9,10] The molecular dimensions of this ligand are not exceptional and the nitrogen atom

(5) Adams, R. D.; Horvath, I. T.; Kim, H. S. *Organometallics* **1984**, *3*, 548.

(6) IR spectra were taken on a Nicolet 5-DXB FT-IR spectrometer in hexane solvent: ν(CO) (cm^{-1}) 2083.9 (m), 2047.1 (s), 2034.7 (m), 2002.9 (s), 1986.4 (m), 1973.7 (w), 1964.6 (w). ^{1}H NMR spectra were run on an IBM NR-80 spectrometer in CDCl$_3$ solvent δ 11.18 (s, br, NCH), 3.64 (d, J_{HH} = 0.8 Hz, NCH$_3$), 3.56 (d, J_{HH} = 0.8 Hz, NCH$_3$), -20.38 (s, br, OsH), -21.18 (s, OsH). Pale yellow crystals of compound **1** were grown by slow evaporation of solvent from cyclohexane solution at -5 °C. These crystals belong to the triclinic space group $P\bar{1}$, *a* = 8.703 (1) Å, *b* = 12.226 (2) Å, *c* = 18.980 (4) Å, α = 85.30 (1)°, β = 78.65 (1)°, γ = 72.29 (1)°, *V* = 1885.7 (7) Å^3, *Z* = 4, ρ_{calcd} = 3.12 g/cm^3. Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer using Mo K$_\alpha$ radiation and the ω-scan technique. Structure-solving calculations were performed on a Digital Equipment Corp. PDP 11/60 computer by using the Enraf-Nonius program library SDP-Plus. The structure was solved by a combination of Patterson and difference Fourier techniques. The data were corrected for absorption (μ_r = 203 cm^{-1}), and the structure was refined by using 3554 reflections (F^2 $\geq$ 3.0σ(F^2)) to yield the final residuals *R* = 0.043 and R_w = 0.052.

(7) Selected interatomic distances (Å) and angles (deg) for **1**: Os(1)–Os(2) = 2.768 (1), Os(1)–Os(3) = 2.911 (1), Os(2)–Os(3) = 2.922 (1), Os(4)–Os(5) = 2.920 (1), Os(4)–Os(6) = 2.918 (1), Os(5)–Os(6) = 2.773 (1), Os(3)–C(20) = 2.026 (15), Os(4)–C(17) = 2.04 (2), C(20)–N(1) = 1.27 (2), C(17)–N(2) = 1.26 (2); Os(3)–C(20)–N(1) = 135 (1), Os(4)–C(17)–N(2) = 136 (1).

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(9) Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348.

(10) Clark, G. R. *J. Organomet. Chem.* **1977**, *134*, 51.

is planar as expected.[10] The carbenoid hydrogen atom, H(1), resonates at a characteristically low-field position, δ 11.8.[9] This ligand was formed evidently by a 1,1 diactivation of CH bonds in one of the methyl groups of the NMe₃ molecule.[11] The hydrogen atoms were transferred to the metal atoms and became the bridging hydride ligands.
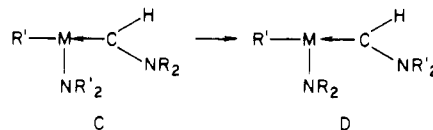
Compound **1** was tested for its ability to promote transalkylation in the archetypical reaction of NEt₃ with N-*n*-Pr₃ (eq 1; R = Et, R′ = *n*-Pr). In a typical reaction 1.0 mL of N-*n*-Pr₃, 0.8 mL of NEt₃, 1.0 mL of MeOH, and 15.0 mg of **1** were heated to 143 ± 3 °C in a Pyrex-sealed tube for 16 h.[13] During this time the solution remained clear and there was no visible evidence of decomposition or precipitate formation. Upon opening the solution was analyzed by GC–mass spectrometry and was found to contain the four tertiary amines NEt₃, NEt₂-*n*-Pr, NEt-*n*-Pr₂, and N-*n*-Pr₃ in the relative amounts 21%, 25%, 26%, and 27%, in addition to the MeOH solvent. The liquid material was removed from the catalyst by vacuum distillation and the residue was separated by TLC on silica plates to yield only four bands. These were identified on the basis of IR and ¹H NMR spectroscopies as three alkyl derivatives of **1** plus **1**. In order of elution they were Os₃-(CO)₈[C(H)NRR′₂](μ-H)₂(μ₃-S), **2** (R = R′ = *n*-Pr), **3** (R = Et, R′ = *n*-Pr), and **4** (R = R′ = Et) in the amounts, **2**, 3.4, **3** 2.8, and, **4**, 4.1 mg.[14] The fourth band was a trace amount (0.8 mg) of **1**.

It is well-known that nucleophiles will attack the electron-deficient carbon atom of coordinated-carbene ligands. In fact, the reaction of primary and secondary amines with heteronuclear carbene complexes has been the most efficient route for the synthesis of amino–carbene complexes.[15] A similar process could provide a rational explanation for the facile transalkylation reaction reported here with tertiary amines. Addition of the tertiary amine NR′₃ to the carbenoid carbon could yield a zwitterionic intermediate like A. The lone pair of electrons on the dialkylamino group NR₂ could then attack the alkyl group R′ causing displacement and formation of the transalkylated intermediate B
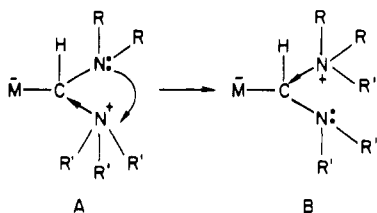
which could then decompose to yield a new carbene ligand and the transalkylated tertiary amine NR₂R′.

Alternatively, a metal-assisted cleavage of a carbon–nitrogen bond of the tertiary amine, such as that proposed by Laine,[16] could lead to an amido–alkyl metal intermediate, C. Interchange of the amido and carbene amino groups, D, followed by reductive elimination of the new tertiary amine would complete the transalkylation.

(11) The reaction of Os₃(CO)₁₂ with NMe₃ at 170 °C gives a low yield of the compound Os₃(CO)₁₀(μ-η²-HC=NMe)(μ-H) which was apparently formed by a 1,1 diactivation of CH groups on one of the CH₃ groups.[12]

(12) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123.

(13) **Caution:** At this temperature the vapor pressures of MeOH and NEt₃ are high and the sealed tubes can explode.

(14) As expected the IR spectra of compounds **2–4** are very similar to that of **1**: for **2** ν(CO)(cm⁻¹), 2083.2 (m), 2046.2 (s), 2032.2 (m), 2002.5 (s), 1986.2 (m), 1970.1 (w), 1963.8 (m); for **3**, 2083.5 (m), 2046.4 (s), 2033.2 (m), 2002.7 (s), 1986.3 (m), 1970.9 (w), 1963.8 (m); for **4**, 2083.6 (m), 2046.4 (s), 2033,7 (m), 2002.7 (s), 1986.3 (m), 1971.6 (w), 1963.6 (m). ¹H NMR spectra were taken in CDCl₃ solvent: for **2** δ 11.15 (s, NCH), 3.50–3.95 (m, C*H*₂CH₂CH₃), 1.52–2.00 (m, CH₂C*H*₂CH₃), 0.80–1.24 (m, CH₂CH₂C*H*₃), −20.32 (s OsH), −21.14 (s, OsH); for **3** 11.24 (s, NCH), 11.14 (s, NCH), 3.42–4.10 (m, C*H*₂CH₂CH₃ and C*H*₂CH₃), 0.80–1.87 (m, CH₂C*H*₃ and CH₂C*H*₃), −20.35 (s, OsH), −21.14 (s, OsH); for **4** 11.23 (s, NCH), 4.02 (q, *J*ₕₕ = 7 Hz C*H*₂CH₃, 3.69 (q, *J*ₕₕ = 7Hz C*H*₂CH₃), 1.47 (t, *J*ₕₕ = 7 Hz, CH₂C*H*₃), 1.31 (t, *J*ₕₕ = 7 Hz, CH₂C*H*₃), −20.35 (br, OsH), 21.13 s, OsH).

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Synthesis of Dicopper(I) [3]Catenates: Multiring Interlocked Coordinating Systems

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Molecules whose topology does not allow planar representation are fascinating.[1] Among them, [2]catenanes,[2,3] consisting of two interlocked rings, and a Möbius strip[4] have been prepared.

We have recently described a template synthesis of interlocked macrocyclic ligands, the catenands.[5,6] We now report that topologically more complex molecules,[7] specifically as [3]catenanes, can be made by taking advantage of the templating effect of copper(I) in 1,10-phenanthroline-based molecular systems. [3]Catenanes have previously been obtained by Schill et al.,[8] following a multistep directed synthesis. The principle of our strategy is represented in Figure 1.

If the linking fragment used in the cyclization step is too short to allow intramolecular ring formation, dimerization leads to a [3]catenane.

The synthesis actually performed is shown in Figure 2.

The starting complex **1⁺** is made according to our previously published procedure,[5] from the corresponding 30-membered ring **8**[9] (see Chart I), the diphenolic derivative of 1,10-phenanthroline[9] and Cu(CH₃CN)₄⁺. Reacting **1⁺** and **2** or **3** in *N,N′*-dimethylformamide (DMF) under high-dilution conditions, in the presence of Cs₂CO₃ (excess), affords poor yields of the dinuclear [3]catenates **4²⁺** (6%) or **5²⁺** (2%). In the course of the reaction, relatively large amounts of monocyclic compounds are also formed. For instance, besides **4²⁺**, the 48-membered ring **6** is obtained (11%); **7** and **8** are isolated in the workup of the reaction mixture leading to **5²⁺**. Interestingly, small amounts of the mixed catenates

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