in $(CH_3)_2SO$ is limited by the low solubility of CO_2 in this solvent and is greater than the K_{CO_2} observed in THF.

It is interesting to note that K_{CO_2} is significantly larger for both salen complexes in the presence of Na^+ than in the presence of Li^+. This is in agreement with the trends in reactivity found by Floriani and co-workers, who attributed the lower reactivity with Li^+ to the greater solvation of this ion by THF.[8b] Experiments with K^+ were not possible due to the low solubility of K^+ electrolytes in THF.

Conclusions

The work described above demonstrates that CO_2 binding to cobalt(I) macrocycle complexes is a general phenomenon that follows predictable trends in metal basicity as reflected by $Co^{II/I}$ redox potentials. Steric factors were found to have a large effect on the binding strength of CO_2 to one cobalt macrocycle complex, suggesting that hydrogen-bonding and/or steric bulk may be important factors in CO_2 binding.

For nonprotic solvents, the strength of CO_2 binding was weakly correlated with solvent dielectric constants. This can be explained to a great extent by the differences in the solvation of CO_2, and ion pairing in the most nonpolar solvents may explain the low binding constants obtained in those solvents. Finally, the role of alkali-metal cations in stabilizing CO_2 adducts of Co(salen) complexes was quantified and was found to be more important for CO_2 binding to these complexes than for CO_2 binding to the cobalt tetraazamacrocycles.

Clusters Containing Carbene Ligands. 7. Preparation of Os3(CO)8[C(H)NMe2](μ3-S)(μ-H)2 and the Nature of Its Reactions with Secondary and Tertiary Amines

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Abstract: $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ were found to react with NMe_3 to yield the complex Os_3-$(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**1a**) in yields of 31% and 26%, respectively. $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ was found to react with H_2S to yield **1a** in 36% yield. Compound **1a** was analyzed by a single-crystal X-ray diffraction analysis and was found to contain a secondary (dimethylamino)carbene ligand terminally coordinated to a sulfur-bridged triosmium cluster. The amino group in the carbene ligand was exchanged by reactions of **1a** with NEt_2H and $NPr_2{}^nH$ at 56 and 80 °C and by reaction with NEt_3 or $NPr_3{}^n$ at 145 °C in MeOH solvent. Significant amounts of $[Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)]^-$ (**3**) are also formed in the latter reactions. The diamine $HN(Et)(CH_2)_2NMe_2$ reacted with **1a** at 80 °C to give $Os_3(CO)_8[C(H)N(Et)(CH_2)_2NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**1e**) in 42% yield. **1e** was decarbonylated at 145 °C to give $Os_3(CO)_7[C(H)N(Et)(CH_2)_2NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2e**) in 41% yield. Compound **2e** was characterized by a single-crystal X-ray diffraction analysis and was found to contain a terminally coordinated $C(H)N(Et)(CH_2)_2NMe_2$ carbene ligand chelated to the cluster through coordination of the NMe_2 group. Labeling studies have shown that the reactions of the carbene complexes with tertiary amines involve C–H activation processes in the alkyl groups and exchange of the amino group of the carbene ligand. A mechanism is proposed that involves iminium ligand intermediates that couple to the carbene ligand to form a nitrogen-containing metallacycle. Solutions of **1a** in methanol were found to catalyze the exchange of alkyl groups between NEt_3 and $NPr_3{}^n$, but analyses of the catalyst mixtures have shown that most of the catalysis was produced by **3**, a decomposition product of the carbene-containing cluster complexes. Crystal data: (for **1a**) space group $P\bar{1}$, $a = 8.703$ (1) Å, $b = 12.226$ (2) Å, $c = 18.980$ (4) Å, $\alpha = 85.30$ (1)°, $\beta = 78.65$ (1)°, $\gamma = 72.29$ (1)°, $R = 0.043$ for 3554 reflections; (for **2e**) space group $P2_1/n$, $a = 11.774$ (3) Å, $b = 12.712$ (2) Å, $c = 14.712$ (4) Å, $\beta = 104.82$ (2)°, $R = 0.050$ for 1866 reflections.

Although amine-substituted carbene ligands, C(R)NR₂ (R = alkyl or aryl), are not uncommon to the field of organometallic chemistry,[1,2] there are still comparatively few examples of polynuclear metal carbonyl complexes containing them.[3] In recent studies, we have discovered that bis(dialkylamino)methanes are effective reagents for the introduction of secondary (dialkylamino)carbene ligands, C(H)NR₂, into a variety of osmium carbonyl cluster complexes through a process that involves the

cleavage of one dialkylamino group and one hydrogen atom from the bis(dialkylamino)methane molecule (e.g., eq 1).[4-6] These carbene complexes possess considerable stability but have been shown to engage in novel multicenter transformation processes in certain cases.[4]

Several years ago, Deeming and Shapley investigated the reactions of NMe_3 with $Os_3(CO)_{12}$, eq 2,[7] and NEt_3 with Os_3-$(CO)_{10}(NCMe)_2$, eq 3,[8] respectively. In this report, we describe

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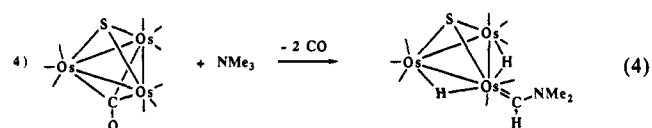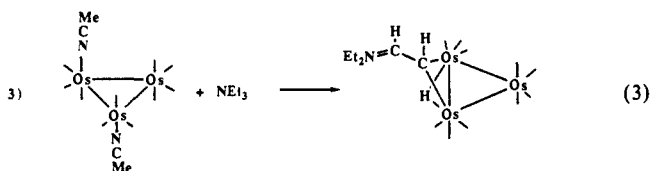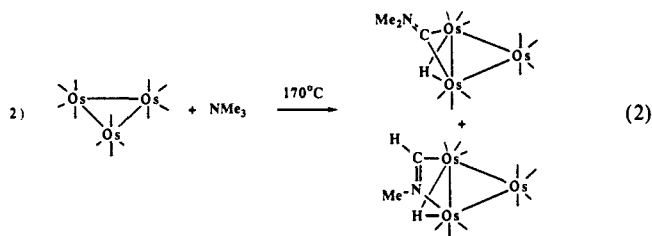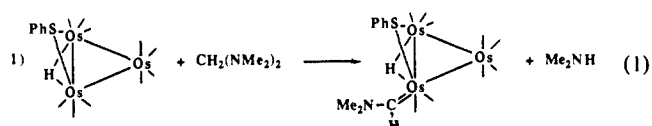(4) Adams, R. D.; Babin, J. E.; Kim, H. S. *J. Am. Chem. Soc.* **1987,** *109,* 1414.

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Clusters Containing Carbene Ligands

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the preparation and reactivity of the complex $Os_3(CO)_8[C(H)$-$NMe_2](\mu_3$-S$)(\mu$-H$)_2$ (**1a**) containing a secondary (dimethyl-amino)carbene ligand. Compound **1a** was obtained initially from the reaction of $Os_3(CO)_9(\mu_3$-CO$)(\mu$-S$)$ with NMe_3, eq 4, but we have also found that it can be obtained directly and more conveniently by the reactions of $Os_3(CO)_{10}(\mu$-SPh$)(\mu$-H$)$ with NMe_3 and $Os_3(CO)_{10}(\mu$-CNMe$_2)(\mu$-H$)$ with H_2S.[9] Reactions (1–4) are each characterized by the activation of aliphatic C–H bonds. In reactions 1 and 2, C–N bonds were also cleaved.

Recently, Laine and co-workers have reported that $Os_3(CO)_{12}$ and certain other metal carbonyl cluster complexes can serve as precursors for catalysts that can produce the metathesis of alkyl groups in tertiary amines, eq 5, under relatively mild conditions

$$NR_3 + NR_3' \rightarrow NR_2R' + NR_2'R \qquad (5)$$
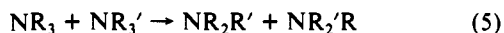
(e.g., 150 °C).[10,11] C–N bond cleavage reactions are required, but evidence was provided to show that the activation of C–H bonds in the alkyl groups also occurred. Unfortunately, no organometallic products that might shed light upon the role of the metal complexes in this reaction were isolated.

Curious to see if the carbene-containing cluster **1a** might also be capable of performing tertiary amine metathesis and if the carbene ligand might be involved in the transformation, we tested **1a** for its ability to produce the exchange of alkyl groups between the amines NEt_3 and NPr_3^n.[9] The results of these studies are also reported here.

Experimental Section

General Methods. Although the reaction products are air stable, all the reactions were performed under an atmosphere of nitrogen, unless otherwise indicated. Technical grade octane was purchased from Philips Co. and purified by treatment with sulfuric acid and distillation before use. Trimethylamine was purchased from Union Carbide Corp. Diethyl-n-propylamine and dimethyl-n-propylamine were purchased from Alfa. Dibutylamine and N,N-dimethyl-N'-ethylethylenediamine were purchased from Aldrich Chemical Co. [^{15}N]Trimethylamine hydrochloride (99% enriched) was purchased from Schwartz/Mann Biotech. Secondary amines, tertiary amines, and methanol were purified and dried by established methods before use. $Os_3(CO)_{10}(\mu$-SPh$)(\mu$-H$)$[12] and

$Os_3(CO)_9(\mu_3$-CO$)(\mu_3$-S$)$,[13] $Os_3(CO)_9(\mu_3$-S$)(\mu$-H$)_2$,[14] PPN$^+$[$Os_3(CO)_9$-$(\mu_3$-S$)(\mu$-H$)$]$^-$,[15] and $Os_3(CO)_{10}(\mu$-CNMe$_2)(\mu$-H$)$[16] were prepared by reported procedures.

GC–mass spectral analyses were performed with the use of a Finnigan Model 4521C spectrometer. IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on an IBM NR-80, a Brüker AM-300 spectrometer, or a Brüker AM-500 spectrometer. ^{2}H NMR spectra were recorded on Brüker WP-200 and AM-300 spectrometers. Elemental analyses were performed at Desert Analytics, Tucson, AZ. TLC separations were performed on plates (0.25-mm Kieselgel 60 F_{254}, from E. Merck, West Germany).

Preparation of Osmium Metal. $Os_3(CO)_{12}$ was placed into a carius tube. The tube was then evacuated and sealed. It was next placed in a furnace, heated to 550 °C, and then allowed to cool slowly. At this point, the sealed tube was completely mirrored. The tube was opened, and the osmium metal was removed by scraping. Its identity was confirmed by powder X-ray diffraction.

Preparation of $Os_3(CO)_8[C(H)NMe_2](\mu_3$-S$)(\mu$-H$)_2$ (1a). Method a. Trimethylamine was slowly passed through a refluxing solution of 15 mg of $Os_3(CO)_9(\mu_3$-CO$)(\mu_3$-S$)$ in 20 mL of octane for 40 min. After the solution was cooled and the solvent removed, the residue was chromatographed by TLC with a CH_2Cl_2/hexane, 2/8, solvent mixture to separate compound **1a** as a very light yellow band; 4.7 mg (31%). Anal. Calcd: C, 14.91; H, 1.01; N, 1.58. Found: C, 15.08; H, 0.94; N, 1.65. IR and ^{1}H NMR spectra of **1a** are listed in Table 1. The mass spectrum showed the parent ion m/e 891 for ^{192}Os and fragments corresponding to the loss of each of eight carbonyl ligands.

Method b. A total of 200 mg (0.21 mmol) of $Os_3(CO)_{10}(\mu$-SPh$)(\mu$-H$)$ and 100 mL of heptane was transferred to a 300-mL Autoclave Engineer's Magne-drive high-pressure reactor (Model No. APB-300). The reactor was sealed and degassed via three pressurization/depressurization cycles with 500 psi of N_2. After the degassing, the reactor was purged with NMe_3 for 20 min, then pressurized to 13 psi with NMe_3, and heated to 162 °C. After the mixture cooled, the solvent was removed in vacuo, and the residue was chromatographed by TLC. The product was eluted as described above. It was recrystallized from the same solvent mixture to yield **1a**, 48 mg (27%).

Method c. Hydrogen sulfide was slowly purged through a refluxing solution of 115.4 mg (0.127 mmol) of $Os_3(CO)_{10}(\mu$-CNMe$_2)(\mu$-H$)$ in 50 mL of n-octane for 8 h. The n-octane solvent was removed in vacuo. Workup as described in method a yielded 40.9 mg of **1a** (36%).

Reactions of 1a with Secondary Amines. (a) With NEt_2H. A 25-mg portion of **1a** was dissolved and the resultant mixture then refluxed in 20 mL of NEt_2H for 1 h. The solvent was removed, and the product was isolated by TLC to yield 20 mg (78%) of $Os_3(CO)_8[C(H)NEt_2](\mu_3$-S$)(\mu$-H$)_2$ (**1b**). Anal. Calcd: C, 17.08; H, 1.42; N, 1.53. Found: C, 17.16; H, 1.32; N, 1.65. IR and ^{1}H NMR spectra of **1b** are given in Table 1.

(b) With NPr_2^nH. A 30-mg portion of **1a** was dissolved in 30 mL of NPr_2H, and the resultant mixture was then heated to 80 °C for 2 h by the use of a constant-temperature oil bath. The product $Os_3(CO)_8[C-(H)NPr_2](\mu_3$-S$)(\mu$-H$)_2$ (**1c**) was isolated in 72% yield by the procedure described above. Anal. Calcd: C, 19.12; H, 1.81; N, 1.41. Found: C, 19.23; H, 1.78; N, 1.52.

(c) With Other Amines. Compounds $Os_3(CO)_8[C(H)NR_2](\mu_3$-S$)$-$(\mu$-H$)_2$ (**1d**, $NR_2 = NEtPr^n$, yield 76%; **1e**, $NR_2 = NEt(CH_2CH_2NMe_2)$, yield 42%; **1f** $NR_2 = NBu_2^n$, yield 25%) were prepared by procedures analogous to that for **1c** with the use of the appropriate secondary amine. Spectra are listed in Table 1.

Reactions of 1a with Tertiary Amines. A solution of 27 mg of **1a**, 0.25 mL of NEt_3, and 1.0 mL of MeOH was sealed in a Pyrex tube and then heated to 145 °C for 30 min. After the solution was cooled, the tube was opened, and the solvent was removed by vacuum distillation. The residue was dissolved in CH_2Cl_2 and was purified by TLC on silica gel to yield **1b**, 11 mg (40%). In a similar manner, compound **1c** was obtained in 56% yield from NPr_3^n.

Preparation of $Os_3(CO)_7[C(H)N(Et)CH_2CH_2NMe_2](\mu_3$-S$)(\mu$-H$)_2$ (2e). A total of 20.0 mg (0.021 mmol) of **1e** was dissolved in 2 mL of MeOH and the mixture sealed under vacuum in a thick-walled Pyrex tube. The tube was heated to 145 °C for 2 h. After the solution cooled, the tube was opened, and the solvent removed under vacuum. The solid

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Table I. Spectroscopic Data

compound	IR: ν, cm^{-1} (hexane)	NMR: δ (CDCl$_3$)
Os$_3$(CO)$_8$[C(H)NMe$_2$](μ_3-S)(μ-H)$_2$ (1a)	2084 (m), 2047 (s), 2035 (m), 2003 (s), 1986 (m), 1974 (w), 1965 (w)	11.18 (s, br) NCH, 3.64 (d, J_{H-H} = 0.8 Hz) NCH_3, 3.56 (d, J_{H-H} = 0.8 Hz) NCH_3, -20.38 (s, br) OsH, -21.18 (s) OsH, 199.20 CHNMe$_2$, 178.39 CO, 178.04 CO, 175.77 CO, 170.84 CO, 170.70 CO, 170.61 CO, 169.51 CO, 166.88 CO, 54.23 NCH_3, 48.65 NCH_3
Os$_3$(CO)$_8$[C(H)NEt$_2$](μ_3-S)(μ-H)$_2$ (1b)	2084 (m), 2046 (s), 2034 (m), 2003 (s), 1986 (m), 1972 (w), 1964 (m)	11.23 (s) NCH, 4.02 (q, J_{H-H} = 7 Hz) CH_2CH$_3$, 3.69 (q, J_{H-H} = 7 Hz) CH_2CH$_3$, 1.47 (t, J_{H-H} = 7 Hz) CH$_2$CH_3, 1.31 (t, J_{H-H} = 7 Hz) CH$_2$CH_3, -20.35 (s) OsH, -21.13 (s) OsH
Os$_3$(CO)$_8$[C(H)NPr$_2$](μ_3-S)(μ-H)$_2$ (1c)	2083 (m), 2046 (s), 2032 (m), 2002 (s), 1986 (m), 1970 (w), 1964 (m)	11.15 (s) NCH, 3.50–3.95 (m) CH_2CH$_2$CH$_3$, 1.52–2.00 (m) CH$_2$CH_2CH$_3$, 0.80–1.24 (m) CH$_2$CH$_2$CH_3, -20.32 (s) OsH, -21.14 (s) OsH
Os$_3$(CO)$_8$[C(H)NEtPr](μ_3-S)(μ-H)$_2$ (1d)	2084 (m), 2046 (s), 2033 (m), 2003 (s), 1986 (m), 1971 (w), 1964 (m)	11.24 (s) NCH, 11.14 (s) NCH, 3.42–4.10 (m) CH_2CH$_2$CH$_3$ and CH_2CH$_3$, 0.80–1.87 (m), CH$_2$CH_2CH$_3$ and CH$_2$CH_3, -20.35 (s) OsH, -21.14 (s) OsH
Os$_3$(CO)$_8$[C(H)NEt(CH$_2$CH$_2$NMe$_2$)]-(μ_3-S)(μ-H)$_2$ (1e)	2083 (m), 2046 (s), 2032 (m), 2002 (s), 1986 (m), 1971 (m), 1963 (m)	11.30 (s, br) NCH, 11.10 (d, J_{H-H} = 2 Hz) NCH, 4.13–3.80 (m) NCH_2CH$_3$, 3.64 (t, J_{H-H} = 6.2 Hz) NCH_2CH$_2$NMe$_2$, 2.75 (t, J_{H-H} = 6.2 Hz) CH$_2$NMe$_2$, 2.48 (t, J_{H-H} = 6.2 Hz) CH_2NMe$_2$, 2.33 (s) NCH_3, 2.23 (s) NCH_3, 1.29 (t, J_{H-H} = 7.2 Hz) NCH_2CH_3, (t, J_{H-H} = 7.2 Hz), -20.32 (br, s) OsH, -21.12 (s) OsH, -21.13 (d, J_{H-H} = 2 Hz) OsH
Os$_3$(CO)$_8$[C(H)NBu$_2$](μ_3-S)(μ-H)$_2$ (1f)	2083 (m), 2046 (vs), 2032 (m), 2002 (s), 1986 (m), 1970 (w), 1964 (m)	11.17 (s) NCH, 3.99 (t) and 3.80 (t) CH_2CH$_2$CH$_2$CH$_3$, 1.89 (m) and 1.60 (m) CH$_2$CH_2CH$_2$CH$_3$, 1.41 (m) and 1.22 (m) CH$_2$CH$_2$CH_2CH$_3$, 1.0 (t) and 0.9 (t) CH$_2$CH$_2$CH$_2$CH_3, -20.23 (s) OsH, -21.10 (s) OsH
Os$_3$(CO)$_7$[C(H)NEt(CH$_2$CH$_2$NMe$_2$)]-(μ_3-S)(μ-H)$_2$ (2e)	2068 (m), 2030 (s), 1983 (s), 1965 (m, br), 1946 (w, sh), 1928 (w, sh)	12.15 (d, J_{H-H} = 2.7 Hz) 3.79–3.49 (m) NCH_2CH$_3$ and NCH_2CH$_2$NMe$_2$, 3.22 (s) NCH$_3$, 3.12 (s) NCH$_3$, 1.34 (t, J_{H-H} = 7 Hz) CH$_2$CH_3, -19.12 (s) OsH, -25.27 (d, J_{H-H} = 2.7 Hz) OsH

was separated by TLC to give 1.5 mg of 1a, 10 mg of 1e (unreacted), and a light yellow band containing 4.0 mg of Os$_3$(CO)$_7$[C(H)N(Et)-CH$_2$CH$_2$NMe$_2$](μ_3-S)(μ-H)$_2$ (2e) (41% based on the amount of 1e consumed). Spectra of 2e are listed in Table I.

Conversion of 1b to 1c. A 28.1-mg (0.0307-mmol) sample of 1b was treated with 0.25 mL of NPr$_3$^{n} and 1.0 mL of MeOH for 1 h at 145 °C in a sealed glass tube. All volatiles were removed in vacuo, and the residue was dissolved in a minimal amount of CH$_2$Cl$_2$ and chromatographed by TLC on silica gel. Elution with a hexane/CH$_2$Cl$_2$, 85/15, solvent mixture yielded 3.3 mg of 1c (11%), 14.6 mg of 1b (52% unreacted), and 4.4 mg of 3.

Studies of the Catalytic Metathesis of Tertiary Amines. General Methods. These reactions were performed either in thick-walled Pyrex sealed tubes or in a Parr Model 4713 high-pressure reaction vessel. The results obtained were independent of the identity of the container. For safety purposes, the Parr vessel is preferred. *At the temperature at which the catalytic studies were performed, the glass containers can, and on occasion did, explode.* All exchange reactions employed NEt$_3$ and NPr$_3$^{n} in equimolar amounts at the start. CH$_3$OH was routinely used as a solvent. It was a requirement. However, products derived from the solvent were never observed. The metathesis reaction did not take place in polar nonprotic solvents (e.g., THF). The sealed reaction containers were inserted into a preheated oil bath at 145 ± 2 °C. All runs were made at least twice to ensure reproducibility. Analyses of the reaction solutions were performed on a Perkin-Elmer Sigma 300 capillary chromatograph equipped with a 37-m methyl silicone fused silica capillary column and a Hewlett-Packard 3390A integrating recorder.

Product Analysis of the Metathesis of NEt$_3$ with NPr$_3$^{n} in Solutions of 1a. In a typical reaction, 0.75 mL of NPr$_3$^{n}, 0.60 mL of NEt$_3$, 1.55 mL of MeOH, and 15 mg of 1a were sealed in a Pyrex tube of 11-mL volume. The reaction vessel was then inserted into a constant-temperature oil bath that was preheated to 145 °C and was maintained at this temperature for 16 h. After the solution cooled, the vessel was opened, and the solution was analyzed by GC–mass spectrometry and found to contain the four amines NEt$_3$, NEt$_2$Pr^n, NEtPr$_2$^{n}, and NPr$_3$^{n} in the relative amounts 33%, 17%, 17%, and 33%, in addition to the MeOH solvent. No other organic products were detected. No precipitate formed, although there was a slight discoloration of the solution during the course of the reaction. The liquid material was removed from the metal complexes by vacuum distillation. The entire residue was dissolved in CDCl$_3$, and the mixture was analyzed by ^{1}H NMR spectroscopy. It was found to contain the three carbene complexes 1b–d and the anion Os$_3$(CO)$_9$-(μ_3-S)(μ-H)$^-$ (3). The cations associated with 3 in these reactions appear to be a mixture of R$_3$NH$^+$ ions, R = Et, Pr^n. There was no evidence for other hydride-containing complexes. The amount of 3 was approximately equal to the sum total of 1b–d. The carbene complexes were then isolated by TLC to yield 1b (3.0 mg), 1c (3.5 mg), and 1d (2.0 mg). The formation of 3 from the carbene complexes was directly dependent on the

reaction time. For example, a reaction mixture analyzed after a period of 4 h showed only a 15% conversion to 3. It was impossible to prevent the formation of 3 in these reactions. The nature of the reaction that leads to the formation of 3 has not been established yet, but the catalytic activity of 3 was investigated independently and is described below.

Reaction of Os$_3$(CO)$_9$(μ_3-S)(μ-H)$_2$ (4) with NEt$_3$ at 25 °C. A total of 15 mg of 4 was added to 5 mL of NEt$_3$ and the resultant mixture stirred at 25 °C for 2 h. The complete conversion of 4 to NEt$_3$H-3 was confirmed by IR spectroscopy.

Determination of Initial Product Formation. A total of 45.7 mg of 1a, 1.0 mL of MeOH, 0.2 mL of NEt$_3$, and 0.25 mL of NPr$_3$^{n} was heated to 145 °C for 15 min in a Pyrex sealed-tube reaction vessel. Analysis of the reaction mixture by GC–mass spectrometry showed the four new tertiary amines in relative amounts: NMe$_2$Et, 8.5%; NMe$_2$Pr^n, 7.1%; NEt$_2$Pr^n, 42.6%; NEtPr$_2$^{n}, 41.8%. TLC separation of the carbene complexes yielded in order of elution 1c (4.8 mg), 1b (8.1 mg), 1a (19.0 mg), and 3 (3.3 mg).

Reaction of 1b with NPr$_3$^{n} in the Presence of 1-Butene. A solution of 46.9 mg of 1b, 0.5 mL of MeOH, 0.2 mL of NPr$_3$^{n}, and 0.2 mL of 1-butene (liquified at -78 °C and transferred by syringe) was sealed in a Pyrex tube and then heated to 145 °C for 3 h. After the solution cooled, the tube was opened, and the liquid was separated by vacuum distillation from the residue. A GC–MS analysis of the liquid showed the formation of NEt$_2$Pr^n and NEtPr$_2$^{n}, but there was no evidence for the formation of NEt$_2$Bu^n.[17]

Investigation of the Catalytic Activity of Decomposition Products Derived from 1a. (a) **General Decomposition.** A total of 15 mg of 1a was placed in a sealed tube and decomposed by heating to 250 °C for 14 h under vacuum. The material inside turned black. The tube was opened, loaded with 1.00 mL of MeOH, 0.40 mL of NEt$_3$, and 0.45 mL of NPr$_3$^{n}, and then sealed and heated to 145 °C in an oil bath for 20 h. GC analysis of the solution showed that there was no more than 3% conversion to the unsymmetric tertiary amines.

(b) **PPN[Os$_3$(CO)$_9$(μ_3-S)(μ-H)] (PPN-3), 3 + (Me$_3$NH)Cl, and Os$_3$(CO)$_9$(μ_3-S)(μ-H)$_2$ (4).** The abilities of PPN-3, Me$_3$NH$^+$Cl$^-$, a mixture of 3 plus Me$_3$NH$^+$Cl$^-$, and Os$_3$(CO)$_9$(μ_3-S)(μ-H)$_2$ (4) to produce catalytic tertiary amine metathesis were determined. A total of 0.0056 mmol of catalyst was used in all of these tests. Turnover frequency (TOF) is defined as

$$\text{TOF} = \frac{\text{moles product}}{\text{moles catalyst/hour}}$$

These tests were conducted in sealed thicked-walled Pyrex tubes of ap-

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(17) Interestingly, small amounts of tertiary amines containing butyl groups were formed in metathesis reactions between NEt$_3$ and NPr$_3$^{n} catalyzed by 3 in the presence of 1-butene.

Table II. Turnover Frequencies (TOF) for Tertiary Amine Metathesis Catalysts at 145 °C in MeOH Solvent[a]

catalyst precursor	product	TOF (± 1)
$[PPN]^+[Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)]^-$	NEt_2Pr	0.0
$1 + Me_3NH^+Cl^-$	NEt_2Pr	13.4
$Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$	NEt_2Pr	13.0
$Me_3NH^+Cl^-$	NEt_2Pt	0.0
osmium metal	NEt_2Pr	0.0
$Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (1a)	NMe_2Pr	1.1[b]
$Os_3(CO)_8[C(H)NEt_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (1b)	NEt_2Pr	0.1[c]

[a] Moles of product/moles of catalyst per hour for reaction NEt_3 + $NPr_3 \rightarrow NEt_2Pr + NPr_2Et$. [b] Estimated from the reaction of 1a with NPr_3^n. [c] Estimated from the reaction of 1b with NPr_3^n.

proximately 11-mL volume. In a typical experiment, 5.0 mg (0.0056 mmol) of 3 was added to a solution consisting of 0.40 mL of NEt_3, 0.50 mL of NPr_3, and 2.00 mL of MeOH. All tests were conducted at 145 °C for a period of 4 h. After the solution cooled, the reaction vessel was opened and analyzed by GC. The results of these tests are listed in Table II.

(c) **Osmium Metal.** A total of 4.5 mg of osmium metal along with 0.4 mL of NEt_3 and 0.5 mL of NPr_3^n was heated at 145 °C for 4 h in a sealed tube. GC analysis of the reaction mixture showed no evidence for the formation of NEt_2Pr^n or $NEtPr_2^n$.

Isotope Labeling Studies. (i) **Incorporation of Deuterium into the Cluster Complex in the Absence of Tertiary Amines.** A total of 42.3 mg of 1f was treated with 2.0 mL of CH_3OD at 145 °C for 10 h in a sealed glass tube. After treatment, the solvent was removed in vacuo, and the residue was chromatographed by TLC. Elution with a hexane/CH_2Cl_2, 8/2, solvent mixture yielded 29.1 mg of 1f, 69%. Compound 1f was analyzed by ^1H NMR and ^2H NMR spectroscopy. The complex was found to contain 82% deuterium in the hydride ligand positions, 23% deuterium in the hydrogen site of the carbene carbon atom, and no deuterium on any of the carbon atoms of the n-butyl groups. These percentages are believed to be accurate to about $\pm 5\%$. Subsequent TLC treatment of this sample of 1f did not lead to any significant changes in the deuterium content or distribution. This sample was used in a reaction with NEt_3 (see section ii below) to test for C–H cleavage processes.

A total of 15.0 mg of 1c was treated with 1.0 mL of CH_3OD for 9 h at 145 °C in a sealed tube. ^1H NMR and ^2H NMR analyses of this sample showed 89% deuterium in the hydride ligand sites, 32% deuterium in the carbene hydrogen site, 9% deuterium on the carbon atoms α to the nitrogen atom, 18% deuterium on the carbon atoms β to the nitrogen atom, and 0% on the carbon atoms γ to the nitrogen atom.

(ii) **Incorporation of Deuterium into the Products in the Course of Metathesis.** The partially deuterated sample of 1f (29.1 mg) prepared in section i was treated with 0.5 mL of CH_3OD and 0.3 mL of NEt_3 for 30 min at 145 °C in a sealed glass tube. All volatile products and remaining reactants were analyzed by GC-MS. The product $NEtBu_2^n$ was found to contain considerable deuterium incorporation: m/e 157, $NEtBu_2^n\text{-}d_0$, 0%; 158, $NEtBu_2^n\text{-}d_1$, 0%; 159, $Bu_2^nNCH_2CD_2H$, 4%; 160, $N(Et\text{-}d_3)Bu_2^n$, 37%; 161, $N(Et\text{-}d_4)Bu_2^n$, 50%; 162, $Bu_2^nNCD_2CD_3$, 7%. The NEt_3 after the reaction was mostly undeuterated: 101, $NEt_3\text{-}d_0$, 91%; 102, $NEt_3\text{-}d_1$, 2%; 103, $NEt_3\text{-}d_2$, 0%; 104, $NEt_3\text{-}d_3$, 8%; 105, $NEt_3\text{-}d_4$, 3%. The residue was dissolved in a minimal amount of CH_2Cl_2 and the mixture chromatographed by TLC on silica gel. Elution with a hexane/CH_2Cl_2, 4/1, solvent mixture yielded 17.1 mg of 1f (59% recovered), 0.7 mg of 1b (3%), and 2.9 mg of 3.

(iii) **Incorporation of Deuterium into the Cluster Complex in the Course of the Exchange of the Dialkylamino Group of the Carbene Ligand.** A partially deuterated sample of 1f (20 mg) containing 81% deuterium in the hydride ligand positions, 25% deuterium in the hydrogen site on the carbene carbon atom, and no deuterium on any of the carbon atoms of the n-butyl groups was converted to 1c in 72% yield by treatment with NPr_3^n (0.5 mL) and CH_3OD (0.5 mL) in a sealed tube at 145 °C for 2.5 h. ^1H NMR and ^2H NMR of the 1c showed 70% deuterium in the hydride ligand sites and 27% deuterium in the carbene hydrogen site. On the propyl group there was 18% deuterium on the carbon atoms α to the nitrogen atom, 34% on the carbon atoms β to the nitrogen atom, and 0% on the carbon atoms γ to the nitrogen atom. The percentages are believed to be accurate to $\pm 5\%$.

(iv) **Reaction of 1b with $^{15}NMe_3$.** $^{15}NMe_3$ was prepared from 0.5 g of $^{15}NMe_3\cdot HCl$ by neutralization with 5.0 mL of 2.0 M NaOH in NaOH in a separate container. The $^{15}NMe_3$ and CH_3OH solvent were then distilled under vacuum into the 45-mL Parr reaction vessel that had been loaded previously with 40.0 mg of 1b. The vessel was then closed and heated to 140 °C for 3 h. After the solution cooled, 5.2 mg of 1a was separated by TLC. A mass spectral analysis of this 1a showed that it contained 100% ^{15}N incorporation into the carbene ligand.

Table III. Crystallographic Data for the Structural Analyses

	compound	
	1a	2e
formula	$Os_3SO_8NC_{11}H_9$	$Os_3SO_7C_{16}H_{18}$
temp (± 3 °C)	23	23
space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.703 (1)	11.774 (3)
b (Å)	12.226 (2)	12.712 (2)
c (Å)	18.980 (4)	14.712 (2)
α (deg)	85.30 (1)	90.0
β (deg)	78.65 (1)	104.82 (2)
γ (deg)	72.29 (1)	90.0
V (Å³)	1885.7 (7)	2128.7 (7)
M_r	885.9	926.8
Z	4	4
ρ_{calc} (g/cm³)	3.12	2.89

Measurement of Intensity Data		
radiation	Mo $K\alpha$ (0.71073 Å)	Mo $K\alpha$ (0.71073 Å)
monochromator	graphite	graphite
detector aperture (mm)		
horizontal ($A + B$ tan θ)	$A = 3.0$	$A = 2.0$
	$B = 1.2$	$B = 0.0$
vert	4.0	2.0
crystal faces	001, 00$\bar{1}$, 1$\bar{1}_7$ 211, 1̄0$\bar{1}$, 011, 0$\bar{1}\bar{1}$, 0$\bar{1}$1	1̄01, 10$\bar{1}$, 0$\bar{1}$1, 01$\bar{1}$, 111, 1̄1̄1̄
cryst size (mm)	0.11 × 0.19 × 0.37	0.04 × 0.19 × 0.23
cryst orientation directn, deg from θ-axis	b,[a] 3.8	[111], 12
reflcns measd	$+h,\pm k,\pm l$	$h,k,\pm l$
max 2θ (deg)	50	48
scan type	moving crystal stationary counter	moving crystal stationary counter
ω-scan width ($A + 0.347$ tan θ)°	1.0	1.1
background	$^1/_4$ addl scan at ea end of scan	$^1/_4$ addl scan at ea end of scan
ω-scan rate (variable)		
max (deg/min)	10.0	4.0[a]
min (deg/min)	1.5	4.0
no. reflcns measd	5002	3659
no. data used with $F^2 \geq 3.0\sigma(F^2)$	3554	1866

Treatment of Data		
absorption correction	applied	applied
coeff (cm⁻¹)	203	191
grid	14 × 14 × 4	10 × 10 × 10
transmissn coeff		
max	0.188	0.503
min	0.087	0.054
P factor	0.03	0.03
final residuals		
R_F	0.043	0.050
F_{wF}	0.052	0.051
	1.97	1.47
largest shift/error value of final cycle	0.02	0.021
largest peak in final diff fourier (e/Å³)	1.81	2.79
no. variables	231	129

[a] Rigaku software uses a multiple-scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to first scan, etc. A maximum of three scans was permitted per reflection.

Crystallographic Analyses. Pale yellow multifaceted plates of 1a were obtained by slow evaporation of solvent from a solution in cyclohexane at −5 °C. Light yellow plates of 2e were obtained from toluene solutions at −10 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements on 1a were made on an Enraf-Nonius CAD4 fully automated four-circle diffractometer. The unit cell was determined and refined from 25 randomly selected reflections obtained from the CAD4 automatic search, center, index, and least-squares routines. Crystal data, data collection, parameters, and results of the analyses are listed in Table III. The data were processed on a Digital Equipment Corp. PDP 11/60 computer with the Enraf-Nonius structure-solving library. Version SDP-PLUS. Neutral atom scattering factors

Table IV. Bond Distances with ESDs for $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (1a)

atoms	distance (Å)	atoms	distance (Å)
Os(1)–Os(2)	2.768 (1)	Os(4)–Os(5)	2.920 (1)
Os(1)–Os(3)	2.911 (1)	Os(4)–Os(6)	2.918 (1)
Os(2)–Os(3)	2.922 (1)	Os(5)–Os(6)	2.773 (1)
Os(1)–S(1)	2.389 (4)	Os(4)–S(2)	2.398 (4)
Os(1)–C(1)	1.84 (2)	Os(4)–C(9)	1.84 (2)
Os(1)–C(2)	1.89 (2)	Os(4)–C(10)	1.82 (3)
Os(1)–C(3)	1.95 (3)	Os(4)–C(17)	2.04 (2)
Os(2)–S(1)	2.385 (5)	Os(5)–S(2)	2.401 (4)
Os(2)–C(4)	1.87 (2)	Os(5)–C(11)	1.89 (2)
Os(2)–C(5)	1.88 (2)	Os(5)–C(12)	1.90 (2)
Os(2)–C(6)	1.87 (2)	Os(5)–C(13)	1.85 (2)
Os(3)–S(1)	2.391 (4)	Os(6)–S(2)	2.383 (5)
Os(3)–C(7)	1.86 (2)	Os(6)–C(14)	1.82 (2)
Os(3)–C(8)	1.91 (2)	Os(6)–C(15)	1.90 (2)
Os(3)–C(20)	2.026 (15)	Os(6)–C(16)	1.88 (2)
C–O(av)	1.16 (2)	C–O(av)	1.17 (2)
C(20)–N(1)	1.27 (2)	C(17)–N(2)	1.26 (2)

were calculated by the standard procedures.[18a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[18b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F^2_o) = [\sigma(I_{raw})^2 + (PF_o)^2]^{1/2}/Lp$.

Compound 1a crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The compound crystallizes with 2 independent molecules in the crystallographic asymmetric unit. The structure was solved by a combination of Patterson and difference Fourier techniques. A numerical absorption correction was applied. Due to the large size of the structure, only the six osmium and two sulfur atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the two carbene carbon atoms were located in a difference Fourier synthesis and were included in the structure factor calculations, but they were not refined. The hydrogen atoms on the methyl groups and the hydride ligands were not located and were not included in the analysis.

Diffraction measurements on 2e were made on a Rigaku AFC6S fully automatic four-circle diffractometer. The unit cell was determined and refined from 25 randomly selected reflections obtained from the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer with the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Compound 2e crystallized in a monoclinic crystal system. The space group $P2_1/c$ was identified on the basis of the systematic absences observed during the collection of the data. The coordinates of the heavy atoms were obtained from a Patterson synthesis. All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All atoms heavier than oxygen were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries. The contributions of all hydrogen atoms were added to the structure factor calculations, but their positions were not refined. The hydride ligands were not located experimentally and were ignored. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. See supplementary material for tables of the anisotropic thermal parameters for 1a and 2e and the structure factor amplitudes for 2e. The structure factor amplitudes for 1a were published previously.[9]

Results

Synthesis of New Aminocarbene Cluster Complexes. The reaction of $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ with NMe_3 at 125 °C resulted in the formation of $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ in 31% yield. However, since $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ is made from $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ by the loss of C_6H_6, attempts were made to obtain 1a directly from the reaction of $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ with NMe_3. From this reaction performed at 162 °C in a high-pressure reactor, 1a was obtained in 27% yield. The reaction of $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ with H_2S at 125 °C also resulted in the formation of 1a in 36% yield. Compound 1a was characterized by IR, ^{1}H NMR, mass spectral, elemental, and a single-crystal X-ray diffraction analyses. The mass spectrum showed
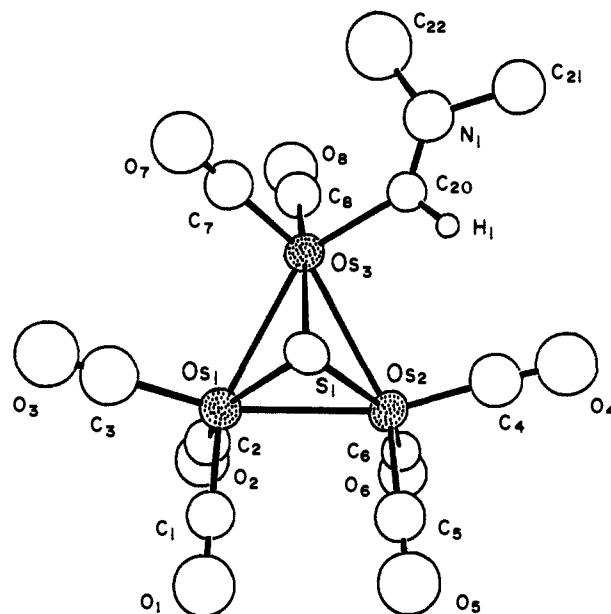

Figure 1. ORTEP drawing of one of the two symmetry-independent molecules found in the crystal of $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (1a).

the parent ion, plus ions corresponding to the loss of each of eight carbonyl ligands.

It is well-known that primary and secondary amines will react with alkoxycarbene complexes to replace the alkoxy group with an amino group.[19] We have found that reactions of 1a with secondary amines at ca. 80 °C will produce an exchange of the amino group of the carbene ligand and yield the new (dialkyl-amino)carbene cluster complexes of $Os_3(CO)_8[C(H)NR_2](\mu_3\text{-}S)(\mu\text{-}H)_2$: 1b ($NR_2 = NEt_2$), 78%; 1c ($NR_2 = NPr_2^n$), 72%; 1d ($NR_2 = NEtPr^n$), 76%; 1e ($NR_2 = N(Et)CH_2CH_2NMe_2$), 42% 1f ($NR_2 = NBu_2^n$), 25%. The observation of two carbene C–H resonances, plus complex patterns for the alkyl groups of 1d and 1e, indicates that these compounds exist in solution as mixtures of two isomers, presumably formed by the two different rotameric conformations about the carbene C–N bond.
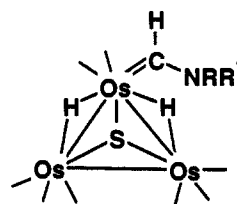
Compound	R R'
1a	Me, Me
1b	Et, Et
1c	Pr, Pr
1d	Et, Pr
1e	Et, $CH_2CH_2NMe_2$

In these complexes, all the metal atoms obey the 18-electron rule; thus, the NMe_2 substituent in 1e is believed to be not associated with a metal atom. However, when heated to 145 °C for 2 h, 1e lost 1 mol of CO and was converted to $Os_3(CO)_7[C(H)N(Et)CH_2CH_2NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (2e) in 41% yield. Compound 2e exists in solution as only one isomer, and its structure was established by an X-ray crystallographic analysis.

Molecular Structures of 1a and 2e. Crystals of 1a contain 2 symmetry-independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP drawing

(18) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

(19) (a) Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, 28, 367. (b) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, 89, 7141.

Clusters Containing Carbene Ligands

J. Am. Chem. Soc.. Vol. 112, No. 9, 1990 3431

Table V. Bond Angles with Esds for
$Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**1a**)

molecule 1		molecule 2	
atoms	angle (deg)	atoms	angle (deg)
Os(2)–Os(1)–Os(3)	61.87 (2)	Os(5)–Os(4)–Os(6)	56.71 (2)
Os(2)–Os(1)–S(1)	54.5 (1)	Os(5)–Os(4)–S(2)	52.6 (1)
Os(2)–Os(1)–C(1)	94.4 (6)	Os(5)–Os(4)–C(9)	114.6 (6)
Os(2)–Os(1)–C(2)	96.7 (5)	Os(5)–Os(4)–C(10)	104.7 (7)
Os(2)–Os(1)–C(3)	159.7 (7)	Os(5)–Os(4)–C(17)	142.7 (5)
Os(3)–Os(1)–S(1)	52.5 (1)	Os(6)–Os(4)–S(2)	52.1 (1)
Os(3)–Os(1)–C(1)	149.6 (6)	Os(6)–Os(4)–C(9)	117.6 (7)
Os(3)–Os(1)–C(2)	108.4 (5)	Os(6)–Os(4)–C(10)	148.0 (7)
Os(3)–Os(1)–C(3)	101.7 (7)	Os(6)–Os(4)–C(17)	92.9 (5)
Os(1)–Os(2)–Os(3)	61.48 (2)	Os(4)–Os(5)–Os(6)	61.59 (2)
Os(1)–Os(2)–S(1)	54.6 (1)	Os(4)–Os(5)–S(2)	52.48 (9)
Os(1)–Os(2)–C(4)	158.5 (7)	Os(4)–Os(5)–C(11)	110.5 (5)
Os(1)–Os(2)–C(5)	95.1 (6)	Os(4)–Os(5)–C(12)	102.4 (6)
Os(1)–Os(2)–C(6)	99.0 (5)	Os(4)–Os(5)–C(13)	149.6 (6)
Os(3)–Os(2)–S(1)	52.4 (1)	Os(6)–Os(5)–S(2)	54.3 (1)
Os(3)–Os(2)–C(4)	101.9 (7)	Os(6)–Os(5)–C(11)	99.7 (5)
Os(3)–Os(2)–C(5)	147.5 (6)	Os(6)–Os(5)–C(12)	157.8 (6)
Os(3)–Os(2)–C(6)	113.4 (5)	Os(6)–Os(5)–C(13)	94.5 (6)
Os(1)–Os(3)–Os(2)	56.65 (2)	Os(4)–Os(6)–Os(5)	61.69 (2)
Os(1)–Os(3)–S(1)	52.4 (1)	Os(4)–Os(6)–S(2)	52.6 (1)
Os(1)–Os(3)–C(7)	100.2 (6)	Os(4)–Os(6)–C(14)	114.8 (6)
Os(1)–Os(3)–C(8)	117.6 (6)	Os(4)–Os(6)–C(15)	146.2 (6)
Os(1)–Os(3)–C(20)	144.4 (5)	Os(4)–Os(6)–C(16)	100.2 (7)
Os(2)–Os(3)–S(1)	52.2 (1)	Os(5)–Os(6)–S(2)	54.9 (1)
Os(2)–Os(3)–C(7)	144.5 (6)	Os(5)–Os(6)–C(14)	100.2 (6)
Os(2)–Os(3)–C(8)	119.8 (6)	Os(5)–Os(6)–C(15)	96.4 (5)
Os(2)–Os(3)–C(20)	92.8 (5)	Os(5)–Os(6)–C(16)	158.4 (7)
Os–C–O(av)	176 (2)	Os–C–O(av)	176 (2)

Table VI. Intramolecular Distances for **2e**[a]

atom–atom	distance	atom–atom	distance
Os(1)–C(11)	1.82 (3)	Os(3)–C(31)	1.75 (3)
Os(1)–C(12)	1.83 (3)	Os(3)–C(1)	1.92 (3)
Os(1)–C(13)	1.84 (3)	Os(3)–N(2)	2.19 (2)
Os(1)–S(1)	2.406 (6)	Os(3)–S(1)	2.405 (6)
Os(1)–Os(2)	2.777 (2)	N(1)–C(1)	1.29 (4)
Os(1)–Os(3)	2.935 (2)	N(1)–C(2)	1.50 (4)
Os(2)–C(22)	1.80 (3)	N(1)–C(4)	1.51 (4)
Os(2)–C(21)	1.84 (3)	N(2)–C(3)	1.50 (4)
Os(2)–C(23)	1.85 (3)	C(2)–C(3)	1.38 (4)
Os(2)–S(1)	2.376 (7)	C(4)–C(5)	1.34 (4)
Os(2)–Os(3)	2.883 (2)	O–C(av)	1.20 (3)

[a] Distances are in angstroms. Estimated standard deviations in the
least significant figure are given in parentheses.

of one of these is shown in Figure 1. The final crystallographic
positional parameters are listed in Table IV. Tables of selected
bond distances and angles are listed in Tables V and VI, re-
spectively. Compound **1a** consists of a closed triangular cluster
of three osmium atoms with a triply bridging sulfido ligand. This
is very similar to the structure of $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**4**).[20]
Compound **1a** contains two hydride ligands, as indicated by the
high-field resonances at –20.38 and –21.18 ppm. The positions
of these ligands were not established directly in the structural
analysis, but they are believed to bridge the metal–metal bonds,
Os(1)–Os(3) and Os(2)–Os(3), which are approximately 0.15 Å
longer than the third Os(1)–Os(2). The bridging hydride ligands
in **4** were observed to bridge the metal–metal bonds that were also
elongated by approximately 0.15 Å. The most interesting ligand
in **1a** is the secondary (dimethylamino)carbene ligand, C(H)-
NMe₂, which is terminally coordinated. The Os–C distance of
2.026 (15) Å [2.04 (2) Å] is very similar to those that have been
reported recently for the secondary (dialkylamino)carbene ligands
in the osmium cluster complexes, $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}
SPh)(\mu\text{-}H)$, 2.02 (2) Å;[4] $Os_3(CO)_8[C(H)NEt_2](\mu_3\text{-}SC_6H_3Me)$-
$(\mu\text{-}H)_2$, 2.03 (2) Å;[4] and $Os_3(CO)_8[C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$,
2.02 (1) Å.[5] The position of the hydrogen atom on the carbene
carbon atom was obtained in a difference Fourier synthesis, but

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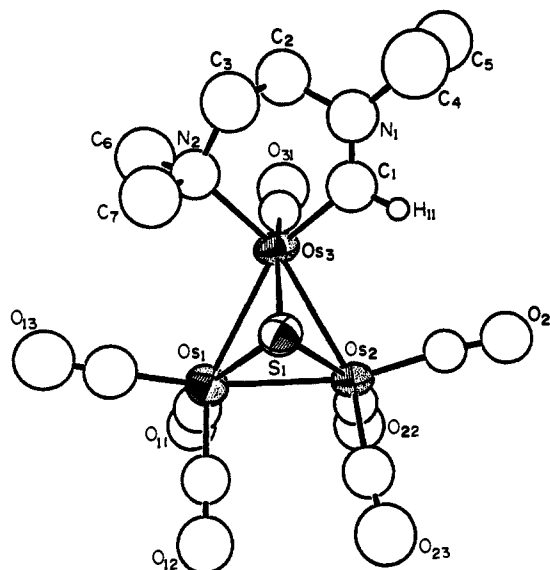
Figure 2. ORTEP diagram of $Os_3(CO)_7[C(H)N(Et)(CH_2)_2NMe_2](\mu_3\text{-}
S)(\mu\text{-}H)_2$ (**2e**) showing 50% probability thermal ellipsoids.

Table VII. Intramolecular Bond Angles for **2e**[a]

atom–atom–atom	angle	atom–atom–atom	angle
C(11)–Os(1)–Os(2)	99 (1)	C(31)–Os(3)–Os(2)	115 (1)
C(11)–Os(1)–Os(3)	109 (1)	C(31)–Os(3)–Os(1)	118.3 (9)
C(12)–Os(1)–Os(2)	91.7 (8)	C(1)–Os(3)–N(2)	90 (1)
C(12)–Os(1)–Os(3)	145.7 (8)	C(1)–Os(3)–S(1)	95.3 (9)
C(13)–Os(1)–Os(2)	164 (1)	C(1)–Os(3)–Os(2)	95 (1)
C(13)–Os(1)–Os(3)	108 (1)	C(1)–Os(3)–Os(1)	146.4 (9)
Os(2)–Os(1)–Os(3)	60.55 (4)	N(2)–Os(3)–Os(2)	148.7 (6)
C(22)–Os(2)–Os(1)	96.0 (8)	N(2)–Os(3)–Os(1)	101.8 (6)
C(22)–Os(2)–Os(3)	108 (1)	Os(2)–Os(3)–Os(1)	57.02 (4)
C(21)–Os(2)–Os(1)	160.9 (8)	C(1)–N(1)–C(2)	118 (3)
C(21)–Os(2)–Os(3)	102.0 (8)	C(1)–N(1)–C(4)	126 (3)
C(23)–Os(2)–Os(1)	95 (1)	N(1)–C(1)–Os(3)	129 (2)
C(23)–Os(2)–Os(3)	148 (1)	C(3)–C(2)–N(1)	108 (3)
Os(1)–Os(2)–Os(3)	62.43 (4)	C(2)–C(3)–N(2)	117 (3)
C(31)–Os(3)–C(1)	91 (1)	O–C(av)–Os	175 (3)
C(31)–Os(3)–N(2)	95 (1)		

[a] Angles are in degrees. Estimated standard deviations in the least
significant figure are given in parentheses.

it was not refined. Additional evidence for the presence of the
hydrogen atom at this site was obtained from the ¹H NMR
spectrum, which showed a very low field resonance, +11.18 ppm,
which is characteristic of these ligands.[4,5,21] There is a very small
long-range coupling (0.8 Hz) of carbene hydrogen atom to the
methyl groups and one of the hydride ligands. The C–N bond
length is characteristically short 1.27 (2) Å [1.26 (2) Å], and
presence of two ¹H NMR signals for the methyl groups indicates
that there is a hindered rotation about the C–N bond.

The natural-abundance ¹³C NMR spectrum of **1a** exhibited
a characteristically low-field resonance at +199.2 ppm for the
carbene carbon atom and eight separate resonances in the region
165–179 ppm for the eight carbonyl ligands; see Table I.

An ORTEP drawing of the molecular structure of **2e** is shown
in Figure 2. The final crystallographic positional parameters are
listed in Table VII. Interatomic bond distances and angles are
listed in Tables VIII and IX. The structure of **2e** is very similar
to that of **1a** and consists of a sulfur-bridged triangular cluster
of three metal atoms. The two elongated metal–metal bonds
signify the location of the two unobserved bridging hydride ligands.
The interesting feature about **2e** is that the NMe₂ group on the
end of the one alkyl group attached to the carbene nitrogen atom
is coordinated to the same metal atom Os(3) that contains the
carbene carbon, Os(3)–N(2) = 2.19 (2) Å. The osmium–carbon
distance to the carbene ligand at 1.92 (3) Å is approximately 0.10

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Table VIII. Bond Distances with Errors for
$Os_3(CO)_7[C(H)N(Et)CH_2CH_2NMe_2](\mu_3$-S$)(\mu$-H$)_2$ (2e)

atoms	distance (Å)	atoms	distance (Å)
Os(1)-C(11)	1.82 (3)	O(11)-C(11)	1.19 (3)
Os(1)-C(12)	1.83 (3)	O(12)-C(12)	1.19 (3)
Os(1)-C(13)	1.84 (3)	O(13)-C(13)	1.22 (3)
Os(1)-S(1)	2.406 (6)	O(21)-C(21)	1.17 (3)
Os(1)-Os(2)	2.777 (2)	O(22)-C(22)	1.25 (3)
Os(1)-Os(3)	2.935 (2)	O(23)-C(23)	1.18 (3)
Os(1)-C(22)	1.80 (3)	O(31)-C(31)	1.21 (3)
Os(2)-C(21)	1.84 (3)	N(1)-C(1)	1.29 (4)
Os(2)-C(23)	1.85 (3)	N(1)-C(2)	1.50 (4)
Os(2)-S(1)	2.376 (7)	N(1)-C(4)	1.51 (4)
Os(2)-Os(3)	2.883 (2)	N(2)-C(7)	1.40 (4)
Os(3)-C(31)	1.75 (3)	N(2)-C(6)	1.47 (4)
Os(3)-C(1)	1.92 (3)	N(2)-C(3)	1.50 (4)
Os(3)-N(2)	2.19 (2)	C(2)-C(3)	1.38 (4)
Os(3)-S(1)	2.405 (7)	C(4)-C(5)	1.34 (4)

Table IX. Bond Angles with Errors for
$Os_3(CO)_7[C(H)N(Et)CH_2CH_2NMe_2](\mu$-S$)(\mu$-H$)_2$ (2e)

atoms	angle (deg)	atoms	angle (deg)
C(11)-Os(1)-C(12)	94 (1)	C(31)-Os(3)-Os(1)	118.3 (9)
C(11)-Os(1)-C(13)	96 (1)	C(1)-Os(3)-N(2)	90 (1)
C(11)-Os(1)-S(1)	151 (1)	C(1)-Os(3)-S(1)	95.3 (9)
C(11)-Os(1)-Os(2)	99 (1)	C(1)-Os(3)-Os(2)	98 (1)
C(11)-Os(1)-Os(3)	109 (1)	C(1)-Os(3)-Os(1)	146.4 (9)
C(12)-Os(1)-C(13)	94 (1)	C(7)-N(2)-C(6)	106 (3)
C(12)-Os(1)-S(1)	95.8 (9)	N(2)-Os(3)-Os(2)	148.7 (6)
C(12)-Os(1)-Os(2)	91.7 (8)	N(2)-Os(3)-Os(1)	101.8 (6)
C(12)-Os(1)-Os(3)	145.7 (8)	N(2)-Os(3)-S(1)	96.8 (6)
C(13)-Os(1)-S(1)	110 (1)	S(1)-Os(3)-Os(2)	52.5 (2)
C(13)-Os(1)-Os(2)	164 (1)	S(1)-Os(3)-Os(1)	52.4 (1)
C(13)-Os(1)-Os(3)	108 (1)	Os(2)-Os(3)-Os(1)	57.02 (4)
S(1)-Os(1)-Os(2)	54.0 (2)	Os(2)-S(1)-Os(3)	74.2 (2)
S(1)-Os(1)-Os(3)	52.4 (2)	Os(2)-S(1)-Os(1)	71.0 (2)
Os(2)-Os(1)-Os(3)	60.55 (4)	Os(3)-S(1)-Os(1)	75.2 (2)
C(22)-Os(2)-C(21)	100 (1)	C(1)-N(1)-C(2)	118 (3)
C(22)-Os(2)-C(23)	96 (1)	C(1)-N(1)-C(4)	126 (3)
C(22)-Os(2)-S(1)	148.6 (9)	C(23)-Os(2)-Os(1)	95 (1)
C(22)-Os(2)-Os(1)	96.0 (8)	O(11)-C(11)-Os(1)	176 (3)
C(22)-Os(2)-Os(3)	108 (1)	O(12)-C(12)-Os(1)	178 (3)
C(21)-Os(2)-C(23)	94 (1)	O(13)-C(13)-Os(1)	178 (3)
C(21)-Os(2)-S(1)	107.5 (8)	O(21)-C(21)-Os(2)	175 (2)
C(21)-Os(2)-Os(1)	160.9 (8)	O(22)-C(22)-Os(2)	172 (3)
C(21)-Os(2)-Os(3)	102.0 (8)	O(23)-C(23)-Os(2)	174 (3)
C(23)-Os(2)-S(1)	95 (1)	O(31)-C(31)-Os(3)	178 (2)
C(23)-Os(2)-Os(3)	148.0 (1)	C(2)-N(1)-C(4)	114 (3)
S(1)-Os(2)-Os(1)	55.0 (1)	C(7)-N(2)-C(3)	104 (3)
S(1)-Os(2)-Os(3)	53.4 (2)	C(7)-N(2)-Os(3)	116 (2)
Os(1)-Os(2)-Os(3)	62.43 (4)	C(6)-N(2)-C(3)	107 (3)
C(31)-Os(3)-C(1)	91 (1)	C(3)-N(2)-Os(3)	109 (2)
C(31)-Os(3)-N(2)	95 (1)	N(1)-C(1)-Os(3)	128 (2)
C(31)-Os(3)-S(1)	166 (1)	C(3)-C(2)-N(1)	107 (3)
C(31)-Os(3)-Os(2)	115 (1)	C(5)-C(4)-N(1)	105 (3)

Å shorter than that in **1a** and may be attributed to a chelation effect brought about by the coordination of the NMe$_2$ group. Other dimensions of the carbene ligand and the cluster are not unusual.

Alkyl Transfer and Exchange of the Amino Group. A most interesting result was the discovery that **1a** reacted with the tertiary amines NEt$_3$ and NPr$_3{}^n$ at 145 °C to form **1b** and **1c** in relatively good yields, 40% and 56%, respectively. This remarkable reaction requires the cleavage of a carbon–nitrogen bond in the tertiary amine. The observation of NMe$_2$Et and NMe$_2$Pr^n from the reaction of **1a** with the mixture of NEt$_3$ and NPr$_3{}^n$ (see below) shows that the alkyl group that was cleaved from the tertiary amine was transferred to the amino group of the carbene ligand and a new tertiary amine was formed. The formation of **1a** containing 100% ^{15}N from the reaction of **1b** with ^{15}NMe$_3$ shows that the carbon–nitrogen bond of the carbene ligand is also cleaved in this exchange reaction. To obtain an estimate of the rate of reaction of **1a** with NPr$_3{}^n$, a reaction was performed in the presence of a

large excess of NPr$_3{}^n$ and was terminated after 30 min. From this reaction, a 56% yield of **1c** was obtained. Compound **1b** was observed to react with NPr$_3{}^n$ to yield **1c**, but this reaction was slower. After 1 h of reaction, the yield of **1c** was only 11%.

To test for the occurrence of C–H bond cleavage processes, the following experiment was conducted. A sample of **1f** was treated with CH$_3$OD at 145 °C for 10 h. Analysis of the recovered **1f** showed approximately 82% deuterium incorporation into the hydride ligand sites, 23% deuterium incorporation into the carbene C–H site, and no detectable incorporation of deuterium at any of the carbon sites of the *n*-butyl groups. Treatment of **1c** yielded similar results, but a significant incorporation of deuterium at the α- and β-carbon atoms of the propyl groups was observed in this case. For this reason, partially deuterated **1f** was used in the following experiments.

The partially deuterated sample of **1f** was allowed to react with N(CH$_2$CH$_3$)$_3$ in CH$_3$OD at 145 °C for 30 min. The reaction period was kept short deliberately to minimize the possibility of side reactions. An analysis of the complexes after reaction showed only a 3% conversion of **1f** to **1b**. Nevertheless, the NBu$_2{}^n$Et product was unambiguously identified by GC–MS spectrometry. The parent ion showed that all of the NBu$_2{}^n$Et contained some deuterium. From an analysis of the parent ion and the fragments formed by methyl cleavage from the ethyl group and propyl cleavage from the butyl groups, the deuterium distribution in the NBu$_2{}^n$Et was assigned as follows: m/e = 157, NBu$_2{}^n$(CH$_2$CH$_3$), 0%; 158, NBu$_2{}^n$(CH$_2$CH$_2$D), 0%; 159, NBu$_2{}^n$(CH$_2$CD$_2$H), 4%; 160, NBu$_2{}^n$(CH$_2$CD$_3$), 37% (this ion may have contained a small amount of NBu$_2{}^n$(CHDCD$_2$H); 161, NBu$_2{}^n$(CHDCD$_3$), 50% (this ion may have contained a small amount of NBu$_2{}^n$(CD$_2$CD$_2$H); 162, NBu$_2{}^n$(CD$_2$CD$_3$), 7%. A mass spectral analysis of the NEt$_3$ after the reaction showed the following ions: 101, NEt$_3$-d_0, 91%; 102, NEt$_3$-d_1, 2%; 103, NEt$_3$-d_2, 0%; 104, NEt$_3$-d_3, 3%; 105, NEt$_3$-d_4, 3%. Corrections for ^{13}C natural abundance were made in determining these deuterium incorporation percentages. The near-absence of deuterium in the unreacted NEt$_3$ indicates that the substantial amounts of deuterium found in the NBu$_2{}^n$Et were introduced during its formation.

A partially deuterated sample of **1f** was converted to **1c** by reaction with NPr$_3{}^n$. Examination of the deuterium content of the **1c** that was formed showed that there is no significant incorporation of deuterium into the metal hydride sites or the hydrogen site on the carbene atom. The latter results imply that the carbene C–H bond is not cleaved in the course of the alkyl transfer and the exchange of the amino group of the carbene ligand.

To test for the possible formation of olefin intermediates, a sample of **1b** was converted to **1c** by reaction with NPr$_3{}^n$ in the presence of 1-butene. As expected, NEt$_2$Pr^n and some NEtPr$_2{}^n$ were formed in this reaction, but there was no evidence for the formation of tertiary amines containing butyl groups.

Catalytic Tertiary Amine Metathesis. Since the carbene-containing clusters **1b** and **1c** also react with tertiary amines, it seemed reasonable to expect that a continuous reaction of this type could produce an alkyl group exchange reaction, eq 5, catalytically. It is known that $Os_3(CO)_{12}$ is a catalyst precursor for reaction 5.[10] Accordingly, the reactions described below were conducted. A reaction mixture consisting of 0.60 mL of NEt$_3$, 0.75 mL of NPr$_3{}^n$, 15 mg of **1a**, and 1.55 mL of MeOH was sealed in an evacuated thick-walled Pyrex tube. The container was heated to 145 °C in an oil bath, and the temperature was maintained for 16 h. During this period, there was no visible formation of precipitate although a slight discoloration of the solution was observed. After the 16-h heating period, the tube was cooled, opened, and analyzed by GC–MS. The liquid was found to consist of the four amines NEt$_3$, NPr$_3{}^n$, NEt$_2$Pr^n, and NEtPr$_2{}^n$ in the relative molar amounts 2:2:1:1. There was no evidence of formation of primary amines, secondary amines, or products derived from the MeOH. The liquid was removed from the nonvolatiles by vacuum distillation. A ^{1}H NMR spectrum of the residue showed the presence of **1b–d** and a quantity of **3** approximately equal to that of the combined amount of **1b–d**. The carbene complexes were separated by TLC

Clusters Containing Carbene Ligands

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to yield **1b**, 3.0 mg; **1c**, 3.5 mg; and **1d**, 2.0 mg.

In an effort to establish the character of the reaction in its initial stages, an experiment similar to the one described above was conducted, except this reaction used 45.7 mg of **1a** and was terminated after 15 min. A GC-MS analysis of the reaction solution showed the formation of the four unsymmetrical tertiary amines NMe$_2$Et (8.5%), NMe$_2$Pr^n (7.1%), NEt$_2$Pr^n (47.6%), and NEtPr$_2$^{n} (41.8%). The relative amounts are scaled so that the combined amount of products is equal to 100%. A separation of the cluster-containing products from this reaction yielded 8.1 mg of **1b**, 4.8 mg of **1c**, 19.0 mg of unreacted **1a**, and 3.3 mg of **3**.

Activity of Decomposition Products. In an experiment designed to measure the catalytic activity of products derived from general decomposition of **1a**, a sample of **1a** was decomposed by pyrolysis at 250 °C under vacuum for a period of 20 h. A black residue formed and was tested for metathesis activity with the standard NEt$_3$/NPr$_3$^{n}/MeOH solutions. However, after 20 h at 145 °C, only a trace (<3% conversion) of the unsymmetrical amines had been formed from this residue. This result indicates that general decomposition does not have significant catalytic activity.

Although we had not observed the formation of osmium metal in these reactions, it was possible that small amounts may have been formed. Therefore, to test for the ability of osmium metal to produce tertiary amine metathesis, a sample was prepared by the pyrolysis of Os$_3$(CO)$_{12}$ at 550 °C. We were unable to produce any detectable tertiary amine metathesis under the conditions of our other reactions with this osmium metal.

A problem of greater concern was the potential activity of decomposition products formed under the milder conditions of actual catalysis. As indicated previously, significant amounts of the anion [Os$_3$(CO)$_9$(μ_3-S)(μ-H)]$^-$ were observed to form during catalysis with the carbene complexes. To evaluate the catalysis of **3**, it was prepared in a pure form as the PPN$^+$ salt.[15] Tests for catalysis by the PPN salt of **3** under the standard conditions showed no activity. However, the counterion of **3** formed from decomposition of the carbene complexes could not be PPN$^+$; thus, other counterions were considered. R$_3$NH$^+$ counterions seemed to be reasonable possibilities. Accordingly, samples of the PPN salt of **3** were combined with Me$_3$NH$^+$Cl$^-$ and were tested for activity. Surprisingly, these mixtures exhibited catalytic activity that was comparable to that of the solutions of the carbene complexes. The turnover frequency for the Me$_3$NH$^+$ salts of **3** was found to be 13.4. As expected, solutions of Me$_3$NHCl in the absence of **3** were catalytically inactive. It was found that the dissolution of Os$_3$(CO)$_9$(μ_3-S)(μ-H)$_2$ (**4**) in NEt$_3$ and NPr$_3$^{n} led to deprotonation and essentially quantitative formation of R$_3$NH-**3**. It was found that the amine solutions of **4** exhibited essentially the same catalytic activity as those prepared from PPN-**3** plus Me$_3$NHCl. This indicates that the catalyst prepared by both methods is probably the same and also indicates that the presence of Cl$^-$ ion in the solutions is not an important factor. Spectroscopic analysis of the catalyst solutions after reaction showed the presence of essentially all of the R$_3$NH-**3**.

Discussion

Os$_3$(CO)$_9$(μ_3-CO)(μ_3-S) was found to react with NMe$_3$ at 125 °C to yield complex **1a**, which contains a secondary (dimethylamino)carbene ligand. The reaction probably occurs by a decarbonylation of the cluster and a ligation of 1 equiv of NMe$_3$ through coordination of the nitrogen atom. Osmium cluster complexes containing NMe$_3$ ligands have been reported.[20,21] In fact, one of these NMe$_3$ complexes was made from the reaction of Os$_3$(CO)$_9$(μ_3-CO)(μ_3-S) with Me$_3$NO·2H$_2$O.[20] The transformation of the NMe$_3$ ligand into the C(H)NMe$_2$ carbene ligand probably occurs by a series of two C-H activation steps at one of the methyl groups. This might begin by a second decarbonylation and a "β-elimination" to yield a π-bonded, iminium ligand H$_2$CNMe$_2$ and a hydride ligand. Isotope-labeling studies have indicated the existence of such β-elimination reactions occurring in tertiary amines on heterogeneous palladium[22] and related metal

carbonyl cluster complexes.[11,23] Presumably, it also occurred in the formation **1a**, in reaction 3,[8] and in the formation RhCl$_3$-(dmso)$_2$(CH$_2$CH=NEt$_2$) from RhCl$_3$(dmso)$_3$ and NEt$_3$.[24] A similar methyl C-H activation was observed in the reaction of 1,8-C$_8$H$_6$(NMe$_2$)$_2$ with RhCl$_3$(dmso)$_3$.[25]

A C-H activation on the CH$_2$ group of the iminium ligand followed by a cleavage of the Os-N bond would complete the formation of the carbene ligand. We have recently observed the transformation of a bridging H$_2$CNMe$_2$ ligand to a bridging HCNMe$_2$ carbene ligand by a metal-induced C-H activation in a related osmium cluster complex[6] and the transformation of C-phenyl-N,N-dimethyliminium ligand into a phenyl(dimethylamino)carbene ligand in the very similar complexes Os$_3$(CO)$_8$-[η^2-Ph(H)C=NMe$_2$](μ_3-S)(μ-H) and Os$_3$(CO)$_8$[C(Ph)-NMe$_2$](μ_3-S)(μ-H)$_2$.[26]

The carbene ligand in **1a** reacts with secondary amines by replacement of the NMe$_2$ group. This reaction is believed to proceed in a fashion similar to that of mononuclear metal complexes that contain carbene ligands.[19] This reaction permitted the synthesis of complexes **1b–f**.

A very interesting result was the preparation of the complexes **1b** and **1c** by the reaction of **1a** with the tertiary amines NEt$_3$ and NPr$_3$^{n}, respectively, although considerably higher temperatures (e.g., 145 °C) and MeOH solvent were required. In this reaction, the alkyl group that was cleaved from the tertiary amine was transferred to the NMe$_2$ group and NMe$_2$Et and NMe$_2$Pr^n were formed.

Important information about the mechanism of the transfer of the alkyl group and exchange of the amino group in this reaction was obtained from the labeling studies. The reaction of **1b** with ^{15}NMe$_3$ to yield **1a** containing 100% ^{15}N showed that the amino group of the carbene ligand was replaced through a cleavage of the carbene C-N bond. The reaction of the partially deuterated **1f** with NEt$_3$ to yield NBu$_2$^{n}Et with deuterium on the α- and β-carbon atoms of the ethyl group established the existence of C-H bond-cleavage processes in the transfer of the ethyl group. The near-absence of deuterium incorporation in the unreacted NEt$_3$ strongly indicates that the C-H bond cleavages occur during the formation of the NBu$_2$^{n}Et and are mechanistically significant. The cleavage of C-H bonds requires involvement of the metal centers since the organic constituents of these reaction mixtures are not capable of producing the necessary C-H bond cleavages. The observation that **1e** is decarbonylated to yield **2e** under conditions similar to those that produce the exchange of the amino group of the carbene ligand with tertiary amines suggests a route for a metal-based activation process of the tertiary amine; see Scheme I. The first step (A) may be simply a replacement of a CO ligand with a NEt$_3$ ligand. Substitution at the carbene-containing metal atom, as in **2e**, would be convenient. C-H activation at the α-carbon atom of the NEt$_3$ ligand could occur by the conventional "β-elimination" mechanism. Either the cleavage of a metal-metal bond, step B, or the loss of a CO ligand, step B', would be required in order to maintain 18-electron configurations at all three metal atoms. These intermediates would contain η^2-iminium ligands, Me(H)C=NEt$_2$. Iminium ligands have been prepared by us in related triosmium cluster complexes.[6,26,27] The reversibility of this β-elimination reaction would allow for the incorporation of deuterium at the α-carbon site of the tertiary amine. The presence of large amounts of deuterium at the methyl carbon atom of the transferred ethyl group implies facile C-H bond activation at that atom also. This could occur by further involvement of the metal atoms, but a simple deprotonation/protonation acid-base reaction is also a possibility. It is known that C-bonded methyl groups on uncoordinated im-

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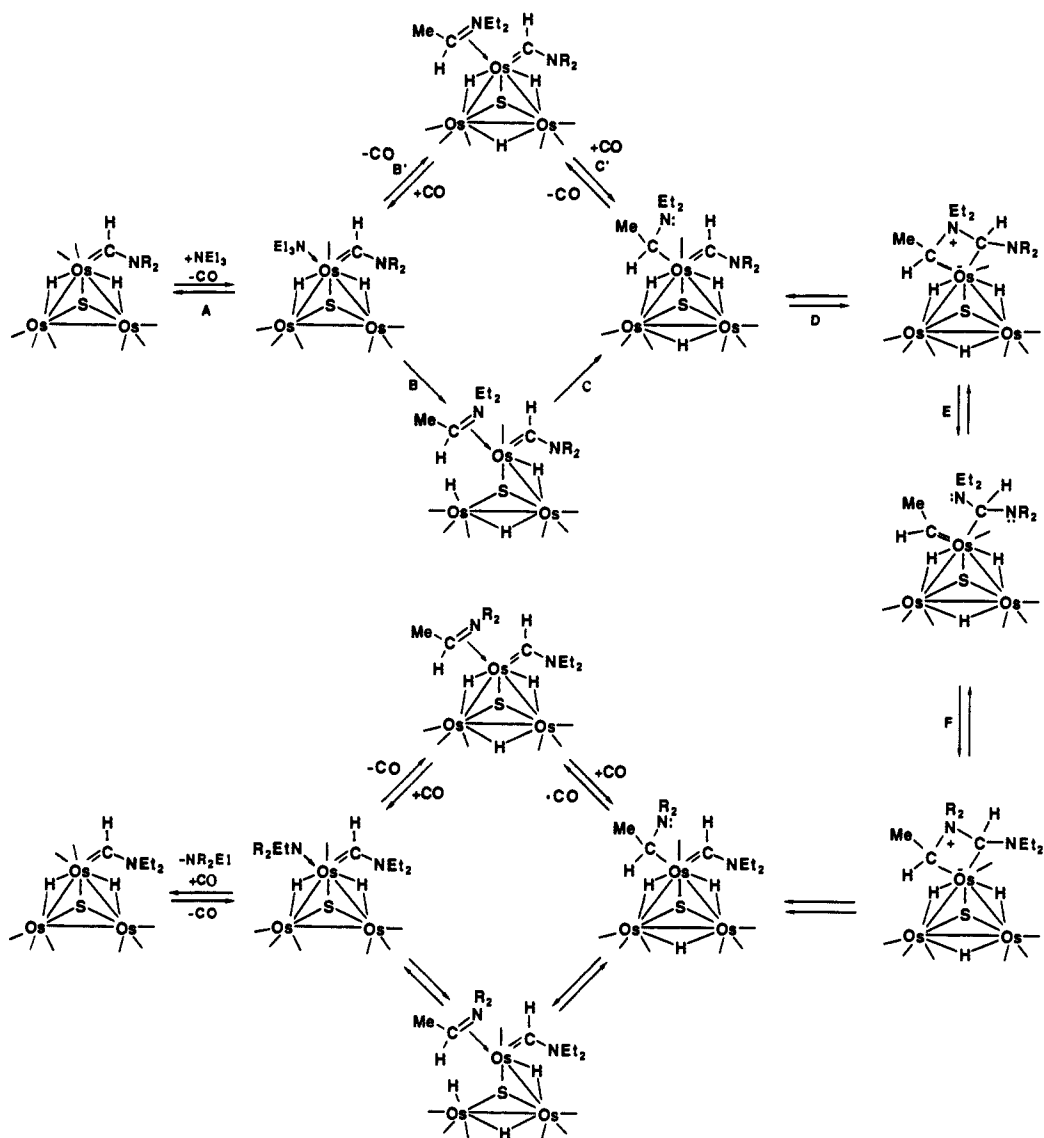
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Scheme I

inium ions undergo a rapid base-induced hydrogen-exchange reaction under very mild conditions.[28] Although the ability of iminium ligands to undergo such an exchange has not been studied, it seems that this should be a viable process under the much more forcing conditions of our reactions. Through these processes, deuterium incorporation at both the α and β sites would be explained. The η^2-iminium ligands in the intermediates could be converted to carbon-coordinated η^1-iminium ligands by either a closure of the cluster, C, or a readdition of CO, C'. η^1-Iminium ligands have been observed previously in mononuclear metal complexes.[29] The uncoordinated electron pair on the nitrogen atom of the η^1-iminium ligand could lead to the formation of a donor–acceptor bond at the electron-deficient carbene carbon atom, step D. This would lead to the formation of a nitrogen-containing metallacycle that could open, step E, to yield an intermediate containing an ethylidene ligand and a (dialkyl-amino)(diethylamino)methyl group. The formation of a new nitrogen-containing metallacycle, step F, by employing the dialkylamino group derived from the carbene ligand would produce the necessary exchange of the amino groups. The E–F transformation proposed here is similar, mutatis mutandis, to the

transformation of metallacyclobutane intermediates as found in the olefin metathesis reaction.[30] The new metallacyclic complex may open to a new η^1-iminium ligand/aminocarbene complex (similar to the reverse of step D), undergo an η^1–η^2 transformation of the iminium ligand (similar to the reverse of steps C or C'), and return one of the hydride (or deuteride) ligands to the iminium ligand to form the new tertiary amine (reverse of B or B'). Replacement of the tertiary amine ligand with a CO ligand would complete the reaction. Clearly, the newly formed carbene complex could undergo a second exchange reaction with another molecule of NR_3, and it occurred to us that these complexes could serve as the basis for a catalytic process that would produce the exchange of alkyl groups between tertiary amines, eq 5. Accordingly, a study of the potential of these carbene complexes to produce this catalysis was conducted. These results are described in the following section.

Catalysis. When a solution consisting of an equimolar amount of NEt_3 and $NPr_3{}^n$ was treated with small amounts of **1a** at 145 °C for 16 h in MeOH solvent, it was converted to a mixture of the four amines NEt_3 (33%), $NPr_3{}^n$ (33%), NEt_2Pr^n (17%), and $NEtPr_2{}^n$ (17%). There were no detectable amounts of any other organic products, including secondary or primary amines or products derived from the MeOH that was used as the solvent. Analysis of the metal-containing compounds showed **1b–d** and **3** in relative amounts that varied depending on the length of the

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reaction time. With long reaction periods, **3** became the dominant species and the amount of **1d** became comparable to that of **1b** and **1c**. With short reaction periods, the relative amounts of **1b** and **1c** were much larger than those of **1d** and **3**.

To evaluate the catalytic activity of **3** and other possible decomposition products, the following materials were prepared: (1) osmium metal by the high-temperature (550 °C) pyrolysis of $Os_3(CO)_{12}$; (2) pyrolytic decomposition of **1a** at 250 °C; (3) PPN-**3**.[15] These three materials were tested for catalytic tertiary amine metathesis with reaction mixtures and under conditions similar to those employed for the solutions of **1a**. The results listed in Table II were negative in each case. However, suspecting that the PPN counterion of **3** was a poor substitute for the anticipated R_3NH^+ ions in the decomposed solutions of **1a**, an additional test with a catalyst prepared from 1:1 mixture of PPN-**3** and [Me_3NH]Cl was performed. Surprisingly, this catalyst mixture had substantial activity and produced tertiary amine metathesis at a rate of 13.4 turnovers/h. [Me_3NH]Cl was tested separately and was found to be inactive. It was found that solutions of **4** in NEt_3 solvent were converted essentially quantitatively to Et_3NH-**3**, and solutions of **4** in the mixed-amine reaction solutions exhibited an activity for catalysis that is essentially the same as the mixtures of PPN-**3** + Me_3NHCl. This finding rules out the Cl^- ion as being important to the catalysis of the mixture of PPN-**3** and [Me_3NH]Cl.

The formations of **1b–d** from the solutions of **1a**, NEt_3, and NPr_3^n and of **1c** from **1b** plus NPr_3^n clearly show that the carbene complexes are capable of performing the catalysis, but since we found it impossible to perform catalysis with the carbene complexes without the formation of some **3**, we have had to use the results of noncatalytic reactions to obtain estimates of the relative reactivity of the carbene complexes toward the tertiary amines.

These evaluations were obtained in the following way. The reaction of **1a** with NPr_3^n at 145 °C produced a 56% conversion to **1c** in a period of 30 min. If the reaction continued at that rate for 1 h, then the conversion to **1c** would be 112%, or in terms of TOF, 1.12. The reaction of **1b** with NPr_3^n at 145 °C produced only an 11% yield of **1c** in 1 h. The corresponding TOF for the formation of NEt_2Pr^n from **1b** is 0.11. In this way, it is estimated that the potential for catalysis by the carbene complexes is only about 0.8–8.0% of the catalytic activity of **3**. The observed activity of **3** is sufficient to account for the bulk of the tertiary amine metathesis observed in the solutions that were initiated with **1a**. There was no evidence for formation of **1b** or **1c** in metathesized solutions of NEt_3 and NPr_3^n when **3** or **4** was used as the catalyst precursor. Thus, it is concluded that carbene complexes **1b–d** are not responsible for tertiary amine metathesis by **3** or **4**. We are not prepared to speculate further as to what the mechanism of catalysis by **3** or **4** might be at this time.

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters for compounds **1a** and **2e** and the mass spectrum of NBu_2^nEt obtained from the reaction of partially deuterated **1f** with NEt_3 in CH_3OD (8 pages); listings of observed and calculated structure factor amplitudes for **2e** (13 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of Some Novel Bis(cyclopentadienyl)silyltitanium(III) Complexes

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Abstract: The complexes $Cp_2Ti(SiHRR')L$ [where L = Et_3P, R = H, and R' = Ph (**5**); L = Me_3P, R = H (**6**), Ph (**7**), and Me (**8**), and R' = Ph] have been prepared as crystalline solids by the reaction of Cp_2TiMe_2 with the appropriate silane in the presence of the phosphine ligand. X-ray structures of **5** and **7** were determined. **7** gave a high-quality structure [R_W = 0.030, monoclinic, $P2_1/n$, a = 8.743 (1) Å, b = 26.192 (5) Å, c = 10.289 (2) Å, β = 100.97 (1)°, Ti–P = 2.609 (1) Å, Ti–Si = 2.652 (1) Å, Si–Ti–P = 84.8 (1)°]. The structure of **5** was also determined [R_W = 0.050, orthorhombic, $P2_12_12_1$, a = 8.312 (4) Å, b = 14.994 (5) Å, c = 17.451 (4) Å], and the refined molecular parameters were indistinguishable from those of **7**. All of the compounds are paramagnetic monomers. Their isotropic EPR spectra in toluene were measured. In each case hyperfine coupling of the unpaired electron to ^{47}Ti, ^{49}Ti, ^{32}P, and ^1H was resolved.

Silyl complexes of the transition elements have attracted interest for many years because of the group analogy between carbon and silicon and because of the effectiveness of certain transition-metal compounds as catalysts for hydrosilylation reactions.[1–4] Early investigations concerned mostly the silyl complexes of electron-rich transition elements because of the relative ease of their preparation.

More recently, a few studies have appeared on compounds of groups 4 and 5 that demonstrate the relevance of such compounds to the catalytic dehydrogenative coupling of organosilanes[5–8] and

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