1216 *Organometallics* 1991, *10*, 1216–1218

# Synthesis and Characterization of Aminomethyl Complexes of Rhenium

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*Received August 28, 1990*

*Summary:* Reductions of rhenium aminocarbene complexes *mer,trans*-M(CO)$_3$(PPh$_3$)$_2$CHNHR$^+$CF$_3$SO$_3^-$ (M = Re; R = CH$_2$Ph, CH(CH$_3$)$_2$; **1a,b**, respectively) by Et$_4$NBH$_4$ have provided complexes bearing aminomethyl ligands *mer,trans*-M(CO)$_3$(PPh$_3$)$_2$CH$_2$NHR (**2a,b**, respectively). Thermolysis of **2a** yields the metal hydride and a small amount of a secondary amine, CH$_3$NHCH$_2$Ph. Borohydride reduction of a related manganese aminocarbene cation (M = Mn R = CH$_2$Ph) afforded the analogous metal hydride and the same secondary amine but no aminomethyl complex. A reaction path involving $\beta$-hydride elimination from an intermediate aminomethyl complex followed by reduction of the resulting imine is proposed to account for the behavior of the manganese complex; the thermolysis of the rhenium complex is thought to follow a similar course.

We recently reported the preparation of secondary aminocarbene complexes of manganese and rhenium by aminolysis of the corresponding methoxycarbene derivatives.[1] Since these complexes are cationic, it occurred to us that it might be possible to reduce the carbene carbon center in them as it is with some methoxycarbene complexes.[2] A literature search revealed no examples of the expected ligand type coordinated to a transition metal, i.e., M–CH$_2$NHR in which a secondary amino group is attached to the alkyl group. There are several examples of compounds having a tertiary amino group bound to coordinated methylene, M–CH$_2$NR$_2$.[3]

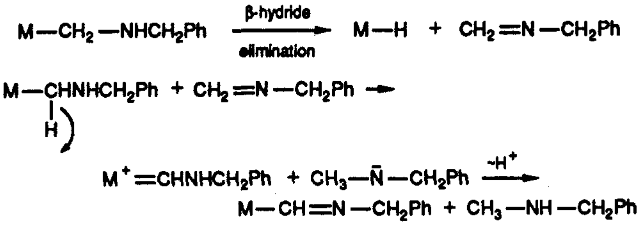
The aminocarbene cations were treated with Et$_4$NBH$_4$ to try to effect their conversion to the corresponding aminomethyl products according to eq 1. The reactions

$$\underset{\textbf{1a,b}}{\text{M=CHNHR}^+\text{CF}_3\text{SO}_3^-} \xrightarrow{\text{Et}_4\text{NBH}_4} \underset{\textbf{2a,b}}{\text{M–CH}_2\text{NHR}} \quad (1)$$

$$\text{M} = \text{Re(CO)}_3\text{(PPh}_3)_2\text{; R} = \text{CH}_2\text{Ph } (\textbf{a}),\ \text{CH(CH}_3)_2\ (\textbf{b})$$

were successful for the synthesis of **2a,b** (92 and 87% yields, respectively). Since organic imines are reduced by metal hydrides to the corresponding amines,[4] this suggested that the corresponding formimidoyl complex, *mer,trans*-Re(CO)$_3$(PPh$_3$)$_2$CHNCH$_2$Ph, could be an alternate source of **2a**; reduction of the formimidoyl complex by Et$_4$NBH$_4$ gave **2a** in good yield. The new compounds have been characterized by elemental analysis and by IR and $^1$H and $^{13}$C NMR spectroscopy (see Experimental Section). The manganese analogue of **1a** (compound **1c**) did not yield the expected aminomethyl product. The manganese complex isolated (in 87% yield) after treatment of **1c** with borohydride was *mer,trans*-Mn(CO)$_3$(PPh$_3$)$_2$H. Also identified in the product mixture was a secondary amine, CH$_3$NHCH$_2$Ph.

Scheme I



M = Re(CO)$_3$(PPh$_3$)$_2$

In order to try to establish the course of the reaction with **1c**, we decided to probe the thermolysis reaction of the (aminomethyl)rhenium complex **2a**. Thermolysis of **2a** afforded *mer,trans*-Re(CO)$_3$(PPh$_3$)$_2$H (in 57% yield) and a small amount of *N*-benzylmethylamine as with **1c**. Thermolysis of **2a** in the presence of an equimolar amount of the rhenium hydride had no effect on the product mixture; thus, a bimolecular reductive elimination does not appear to account for the secondary amine product. It has been suggested previously[5] that $\beta$-hydride elimination from nitrogen in decompositions of putative intermediate diaminomethyl complexes might be responsible for metal hydride formation. With our aminomethyl complexes $\beta$-hydride elimination would be expected to yield *N*-benzylformaldimine, in addition to the observed hydrides, and not the secondary amine. We suggest that the amine is formed by a secondary reaction involving hydride abstraction from the rhenium aminomethyl complex by the imine, followed by proton transfer, as shown in Scheme I. Hydride donation, from the $\alpha$-carbon atom, has been demonstrated for alkoxymethyl complexes,[6] and it is known that strong bases will deprotonate the aminocarbene complexes.[1] The thermal instability of the imine[7] precludes our being able to test the proposed hydride abstraction step. Thermolysis of the rhenium formimidoyl complex[1] yields the same rhenium hydride also (see Experimental Section); the organic products of this reaction are not yet known.

The yield of the manganese hydride complex formed in the attempted reduction of **1c** is much higher than that of the rhenium hydride formed from thermolysis of **2a**. This may be due to the borohydride that is available as an additional reducing agent for the intermediate imine, so that sacrificial hydride transfer from the aminomethyl product is not required. Alternatively, the thermolysis of the aminomethyl and formimidoyl complexes may simply occur more efficiently than with the rhenium complex. The apparent thermal lability of the aminomethyl manganese complex as compared to other first-row transi-

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[1] Gibson, D. H.; Mandal, S. K.; Owens, K.; Richardson, J. F. *Organometallics* **1990**, *9*, 1936.

[2] Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics*, in press.

[3] (a) Fong, C. W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100. (b) Sepelak, D. J.; Pierpondt, C. G.; Barefield, E. K.; Budz, J. T.; Poffenberger, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 6178. (c) Barefield, E. K.; Sepelak, D. J.; *J. Am. Chem. Soc.* **1979**, *101*, 6542.

[4] See: Hudlicky, M. *Reductions in Organic Chemistry*; Halsted Press, John Wiley and Sons: New York, 1984; p 132 and references cited therein.

[5] Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1583.

[6] (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Davies, S. G.; Maberly, T. R. *J. Organomet. Chem.* **1985**, *296*, C37.

[7] See: McDonagh, A. F.; Smith, H. E. *J. Org. Chem.* **1968**, *33*, 8 and references cited therein.

0276-7333/91/2310-1216$02.50/0

tion-metal complexes with tertiary aminomethyl substituents[3] may be attributed to the lack of an available $\beta$-hydride elimination pathway for the latter compounds.

## Experimental Section

**General Data.** Pentane was dried over concentrated $H_2SO_4$ and fractionally distilled. Reagent grade dichloromethane was used as received. Reagent grade methanol and acetonitrile were dried over type 3A molecular sieves. Isopropylamine, $CD_2Cl_2$, and $CD_3CN$ were obtained from Aldrich and used directly. $Et_4NBH_4$ was prepared by a method described previously.[8] The organometallic starting materials *mer,trans*-$Re(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$, *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHNCH_2Ph)^+CF_3SO_3^-$, *mer,trans*-$Re(CO)_3(PPh_3)_2(CHNHCH_2Ph)^+CF_3SO_3^-$, and *mer,trans*-$Re(CO)_3(PPh_3)_2(CHNCH_2Ph)$ were prepared as previously reported.[1] Spectroscopic measurements were obtained on the following instruments: $^1H$ NMR, Varian XL-300 and EM-390; $^{13}C$ NMR, Varian XL-300; IR, Perkin-Elmer 599B and Nicolet SX170. $^1H$ and $^{13}C$ NMR chemical shifts were referenced to tetramethylsilane. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All reactions were performed under an atmosphere of prepurified nitrogen.

***mer,trans*-$Re(CO)_3(PPh_3)_2(CH_2NHCH_2Ph)$ (2a). (a) By Reduction of *mer,trans*-$Re(CO)_3(PPh_3)_2(CHNHCH_2Ph)^+CF_3SO_3^-$ (1a).** To a stirred solution of **1a** (0.10 g, 0.094 mmol) in $CH_3OH$ (10 mL) at room temperature was added $Et_4NBH_4$ (0.014 g, 0.094 mmol). After 5 min, a white precipitate began to form; after 30 min, the solvent was evaporated from the mixture. The residue was scraped from the sides of the flask and stirred with 30 mL of water for 5 min. The residue was then collected by filtration and dried, in vacuo, to yield 0.079 g (92%) of product, mp 159–160 °C. Efforts to recrystallize the product resulted in slight decomposition and lower yield; analytical data were obtained on the crude product. Anal. Calcd for $C_{47}H_{40}NO_3P_2Re$: C, 61.70; H, 4.41; N, 1.53. Found: C, 61.66; H, 4.46; N, 1.33. IR ($CH_2Cl_2$) $\nu_{CO}$ 2015 (vw), 1923 (s), 1884 (m) $cm^{-1}$. IR (neat, DRIFTS): $\nu_{NH}$ 3348 (w) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.35 (m), 2.93 (s), 2.08 (t, $J_{PH}$ = 7.3 Hz), 0.45 (s, br). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 199.0 (t, $J_{PC}$ = 9.2 Hz), 196.1 (t, $J_{PC}$ = 7.5 Hz), 142.2 (s), 135.8 (t, $J_{PC}$ = 23.4 Hz), 133.8 (t, $J_{PC}$ = 5.6 Hz), 130.1 (s), 128.4 (s), 128.4 (t, $J_{PC}$ = 4.6 Hz), 128.1 (s), 126.3 (s), 63.2 (s), 28.9 (t, $J_{PC}$ = 6.4 Hz).

**(b) By Reduction of *mer,trans*-$Re(CO)_3(PPh_3)_2(CHNCH_2Ph)$.** To a stirred solution of *mer,trans*-$Re(CO)_3(PPh_3)_2(CHNCH_2Ph)$ (0.12 g, 0.13 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C was added $Et_4NBH_4$ (0.019 g, 0.13 mmol). After 50 min, the volume of the solvent was reduced on a rotary evaporator, $CH_3OH$ (20 mL) was added, and the solution was chilled to −20 °C to precipitate the product. White crystals were collected by filtration and dried for 2 h under vacuum to give 0.080 g (67%) of **2a**. The spectral properties of the product were identical with those above.

***mer,trans*-$Re(CO)_3(PPh_3)_2[CHNHCH(CH_3)_2]^+CF_3SO_3^-$ (1b).** To 15 mL of $CH_2Cl_2$ containing *mer,trans*-$Re(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$ (0.40 g, 0.40 mmol) and maintained at 0 °C was added isopropylamine (34 $\mu$L, 0.40 mmol) dropwise from a syringe with stirring. The reaction was complete after 5 min at which time 10 mL of pentane was added, and the solution was chilled to −20 °C overnight. White crystals were collected by filtration, washed with 10 mL of pentane, and dried, in vacuo, to give 0.37 g (90%) of product, mp 213–214 °C dec. Anal. Calcd for $C_{44}H_{39}F_3NO_6P_2ReS$: C, 52.07; H, 3.87; N, 1.38. Found: C, 52.14; H, 3.86; N, 1.30. IR ($CH_2Cl_2$): $\nu_{CO}$ 2060 (w), 1960 (s), 1935 (sh) $cm^{-1}$. IR (neat, DRIFTS): $\nu_{NH}$ 3231 (m) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 10.2 (d, br, $J_{HH}$ = 21.0 Hz), 10.0 (d, $J_{HH}$ = 21.0 Hz), 7.5 (m), 2.9 (hep, $J_{HH}$ = 6.6 Hz), 0.55 (d, $J_{HH}$ = 6.6 Hz). At this point, the broad doublet at lower field was assigned to the NH group while the sharper doublet at $\delta$ 10.0 was assigned to the isopropyl methine group. These assignments were confirmed by an NMR experiment using $CD_3CN$ as the solvent. In $CD_3CN$, the doublet assigned to the methine proton becomes the lower field resonance while the broad doublet assigned to the NH group moves slightly upfield. When a drop of $D_2O$ was added to this NMR sample, the lower field doublet collapsed to a singlet and the other low-field doublet disappeared. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 222.3 (t, $J_{PC}$ = 9.0 Hz), 194.6 (t, $J_{PC}$ = 6.3 Hz), 191.5 (t, $J_{PC}$ = 8.6 Hz), 134.0 (t, $J_{PC}$ = 24.6 Hz), 133.3 (t, $J_{PC}$ = 5.6 Hz), 131.2 (s), 129.3 (t, $J_{PC}$ = 5.0 Hz), 63.3 (s), 21.5 (s).

***mer,trans*-$Re(CO)_3(PPh_3)_2[CH_2NHCH(CH_3)_2]$ (2b).** To a stirred solution of **1b** (0.30 g, 0.30 mmol) in $CH_3CN$ (15 mL) at room temperature was added $Et_4NBH_4$ (0.043 g, 0.30 mmol). A white precipitate began to form immediately. After 5 min, the product was collected and dried in vacuo to yield 0.22 g (87%), mp 216 °C dec. Anal. Calcd for $C_{43}H_{40}NO_3P_2Re$: C, 59.57; H, 4.65; N, 1.62. Found: C, 58.89; H, 4.67; N, 1.82. IR ($CH_2Cl_2$): $\nu_{CO}$ 2015 (vw), 1920 (s), 1885 (m) $cm^{-1}$. IR (neat, DRIFTS): $\nu_{NH}$ 3290–3340 (vw, br) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, −4 °C): $\delta$ 7.50 (m), 1.96 (t, $J_{PH}$ = 6.6 Hz; the NH proton is thought to underlie this triplet as it is broadened; this assignment is supported by the integration), 1.51 (hep, $J_{HH}$ = 6.1 Hz), 0.50 (d, $J_{HH}$ = 6.1 Hz). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, −4 °C): $\delta$ 198.8 (t, $J_{PC}$ = 9.4 Hz), 195.4 (t, $J_{PC}$ = 6.8 Hz), 135.4 (t, $J_{PC}$ = 23.2 Hz), 133.6 (t, $J_{PC}$ = 5.4 Hz), 129.9 (s), 128.3 (t, $J_{PC}$ = 4.6 Hz), 56.6 (s), 24.7 (t, $J_{PC}$ = 5.9 Hz), 22.0 (s).

**Thermolysis of *mer,trans*-$Re(CO)_3(PPh_3)_2(CH_2NHCH_2Ph)$ (2a).** (a) A sample of **2a** (0.025 g, 0.027 mmol) was placed in a Schlenk tube and stoppered. The sample was heated at 170 °C and then allowed to cool to 150 °C; after 2 h at 150 °C, the sample was cooled to room temperature. The flask was opened, and the residue was triturated with pentane. The major pentane-soluble product was identified as $CH_3NHCH_2Ph$ by comparison of the NMR spectrum with that of an authentic sample. The pentane-insoluble residue was chromatographed on a florisil column with $CH_2Cl_2$/pentane (9:1). The first fractions off the column contained only *mer,trans*-$Re(CO)_3(PPh_3)_2H$ (0.12 g, 57% yield) identified by comparison of its spectral properties with those of an authentic sample.[9] Additional carbonyl-containing products were then eluted, in very small amounts; these products have not been identified.

(b) A second experiment was conducted by using equimolar amounts of **2a** and *mer,trans*-$Re(CO)_3(PPh_3)_2H$. Again, the major organic product was identified as $CH_3NHCH_2Ph$, and the major metal carbonyl product was *mer,trans*-$Re(CO)_3(PPh_3)_2H$. No difference in product distributions were observed (after correction for the added hydride) in comparing this experiment with the one above.

**Attempted Reductions of *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHNHCH_2Ph)^+CF_3SO_3^-$ (1c).** To 25 mL of $CH_2Cl_2$ containing **1c** (0.50 g, 0.58 mmol) at room temperature was added $Et_4NBH_4$ (0.083 g, 0.58 mmol). After 5 min, the solvent was removed and the residue triturated with pentane. The pentane extracts smelled strongly of amine and showed no carbonyl stretching bands in the IR spectrum. A $^1H$ NMR study of the pentane-soluble portion in $CD_2Cl_2$ showed a complicated spectrum. However, the major product was determined to be $CH_3NHCH_2Ph$ by comparison of the NMR spectrum with that of the authentic sample. The pentane-insoluble product was dissolved in $CH_2Cl_2$, the solution was mixed with decolorizing charcoal and filtered through Celite, and the volume of the solvent was reduced. Pentane was added until the solution became slightly cloudy, and this was chilled to −20 °C overnight. Pale yellow crystals of *mer,trans*-$Mn(CO)_3(PPh_3)_2H$ were collected and dried, in vacuo, to yield 0.32 g, 82%. The hydride complex was identified by comparison of its spectral properties with those of an authentic sample.[10] Doing this reaction at −78 °C gave similar results as did changing the solvent to $CH_3OH$ or $CH_3CN$. When half of 1 molar equiv of $Et_4NBH_4$ was used, only half of the starting material reacted, but the same products were formed.

**Thermolysis of *mer,trans*-$Re(CO)_3(PPh_3)_2(CHNCH_2Ph)$.** A sample of *mer,trans*-$Re(CO)_3(PPh_3)_2(CHNCH_2Ph)$ (0.073 g, 0.093 mmol) was placed in a Schlenk tube and stoppered. The sample was heated to 170 °C and then allowed to cool to 150 °C. This temperature was maintained for 2 h, during which time the

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[8] Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *J. Organomet. Chem.* **1981**, *218*, 325.

[9] Flitcroft, N.; Leach, J. M.; Hopton, F. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 137.

[10] Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 2933.

white sample melted and became yellow. After 2 h, the sample was allowed to cool to room temperature. NMR and IR spectral data confirm that the major metal carbonyl product is *mer,-trans*-$Re(CO)_3(PPh_3)_2H$ (by comparison of its spectral properties with those of an authentic sample).

**Acknowledgment.** Support of this work by the National Science Foundation (Grant RII-8610671) and the Commonwealth of Kentucky (EPSCoR Program) is gratefully acknowledged. Partial support of this work by the Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), is also gratefully acknowledged.

# *Additions and Corrections*

Jeffrey W. Freeman and Fred Basolo*: Kinetics and Mechanisms of Ligand Substitution Reactions of the Vanadium Triad Metals. Syntheses and Reactivities of $(\eta^5\text{-}C_5H_5)M(CO)_3(C_4H_8E)$ (M = Nb, E = S, Se, Te; M = Ta, E = S). **1991**, *10*, 256–263.

On column 2, line 4 of page 256 the sentence beginning with "Equilibria studies..." should be replaced with "Studies of $ReBr(CO)_3(EMe_2)_2$, $(Cp\text{-}Me)Mn(CO)_2EMe_2$, and $CpV(CO)_3EMe_2$ showed[11] that the stability of these complexes increases in the order S < Se < Te." To ref 11 add the following: Belforte, A.; Calderazzo, F.; Vitali, D.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1985**, *115*, 125.