Bis(cyclopentadienyl)methane-Bridged Dinuclear Complexes, 10[◇]

The Bis(cyclopentadienyl)methane Link between Lewis Basic and Lewis Acidic Metal Centers☆

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Received May 2, 1995

Key Words: Bis(cyclopentadienyl)methane / Heterobimetallic complexes / Imido complexes

The mononuclear rhodium complexes $[(C_5H_5CH_2C_5H_4)Rh(CO)_2]$ (**1**) and $[(C_5H_5CH_2C_5H_4)Rh(PhC{\equiv}CPh)(PiPr_3)]$ (**2**) readily react with *n*BuLi or TlOEt to yield the corresponding lithium salts **3** and **4** or thallium salts **5** and **6**. The reaction of these salts with $[(C_5H_5)Nb(NtBu)Cl_2]$ (**7**) leads to the formation of the heterodinuclear compounds $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{(C_5H_5)Nb(NtBu)Cl\}]$ (**8**) and $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(PiPr_3)\}\{(C_5H_5)Nb(NtBu)Cl\}]$ (**9**), respectively. Treatment of **3**–**6** with $[Mo(NtBu)_2Cl_2]$ (**10**) gives the heterodinuclear Rh/Mo complexes $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{Mo(NtBu)_2Cl\}]$ (**11**) and $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(PiPr_3)\}\{Mo(NtBu)_2Cl\}]$ (**12**). The analogous reaction of $[Mo(NMes)_2Cl_2(DME)]$ (**13**) with **3**–**6** yields the corresponding complexes $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{Mo(NMes)_2Cl\}]$ (**14**) and $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(PiPr_3)\}\{Mo(NMes)_2Cl\}]$ (**15**). From the monometallated ligand $[(C_5H_5CH_2C_5H_4)M]$ (M = Li: **16**; M = Tl: **17**) and the imidometal compounds **7**, **10** and **13**, the mononuclear complexes $[(C_5H_5CH_2C_5H_4)(C_5H_5)Nb(NtBu)Cl]$ (**18**) and $[(C_5H_5CH_2C_5H_4)Mo(NR)_2Cl]$ (R = *t*Bu: **19**; R = Mes: **20**) have been obtained.

Continuing our research in the field of dinuclear complexes, we recently established a synthetic route to *hetero*bimetallic compounds bridged by the bis(cyclopentadienyl)methane dianion[1]. Since complexes containing two or more *different* metal atoms have attracted major interest because of their potential cooperative behaviour[2], we attempted the synthesis of binuclear complexes bearing a nucleophilic rhodium center and a second metal center with a d^0 configuration. We focussed our effort in particular on relatively electron-poor imido complexes because of the well known electronic *flexibility* of the imido ligand[3]. Accordingly, we planned to generate a heterobimetallic environment for metal-mediated coupling reactions of π-basic ligands, for example, NR^{2-} coordinated to a π-acidic d^0 complex fragment and π-acidic ligands coordinated to a d^8 rhodium (or any other electron-rich metal) center of pronounced metal basicity. The chemistry of d^8 metal bases (phosphane and carbonyl half-sandwich type complexes with M = Co, Rh, Ir)[4] and d^0 metal acids (oxo and imido complexes with M = Nb, Mo, W)[5] has not been examined in this context so far.

In this paper we describe our initial results with particular emphasis on the preparation of Rh/Nb and Rh/Mo bimetallic complexes. Furthermore, we report the synthesis of mononuclear Nb and Mo half-sandwich type complexes containing a dangling noncoordinated Cp-unit as substituent, which can also be used as building blocks for heterobimetallic compounds.

[◇] Part 9: B. Stempfle, H. Werner, *Gazz. Chim. Ital.*, **1995**, *125*, in press.

Preparation of Binuclear Rh/Nb Complexes

The well known rhodium compounds $[(C_5H_5CH_2C_5H_4)Rh(CO)_2]$ (**1**)[6] and $[(C_5H_5CH_2C_5H_4)Rh(PhC{\equiv}CPh)(PiPr_3)]$ (**2**)[7] readily react with *n*BuLi to give the corresponding lithium salts **3** and **4**. The analogous thallium salts **5** and **6** can also easily be prepared by reacting **1** or **2** with one equivalent of TlOEt in ether. Whereas the lithium salts are very air- and moisture-sensitive and have to be prepared just before use, the thallium salts may be handled without any problems by Schlenk tube techniques and can be stored under argon at −78 °C for several days.

Reaction of the salts **3**–**6** with $[(C_5H_5)Nb(NtBu)Cl_2]$ (**7**) yields the expected heterobimetallic complexes $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{(C_5H_5)Nb(NtBu)Cl\}]$ (**8**) and $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(PiPr_3)\}\{(C_5H_5)Nb(NtBu)Cl\}]$ (**9**) in good yields (Scheme 1). Both compounds **8** and **9** are obtained as yellow oils which are soluble in most common organic solvents and have been characterized by spectroscopic methods and elemental analysis. They can be stored under argon at −78 °C for weeks but slowly decompose at room temperature or in solution.

Preparation of Binuclear Rh/Mo Complexes

When the lithium or thallium salts **3**–**6** are treated with $[Mo(NtBu)_2Cl_2]$ (**10**) at −78 °C in THF, the heterodinuclear Rh/Mo complexes $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{Mo(NtBu)_2Cl\}]$ (**11**) and $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(PiPr_3)\}\{Mo(NtBu)_2Cl\}]$ (**12**) are obtained almost quantitatively (Scheme 2). The spectroscopic data of **11** and **12**, which were isolated as red-orange, slightly air-sensitive oils, and the elemental analyses confirm the structures proposed for

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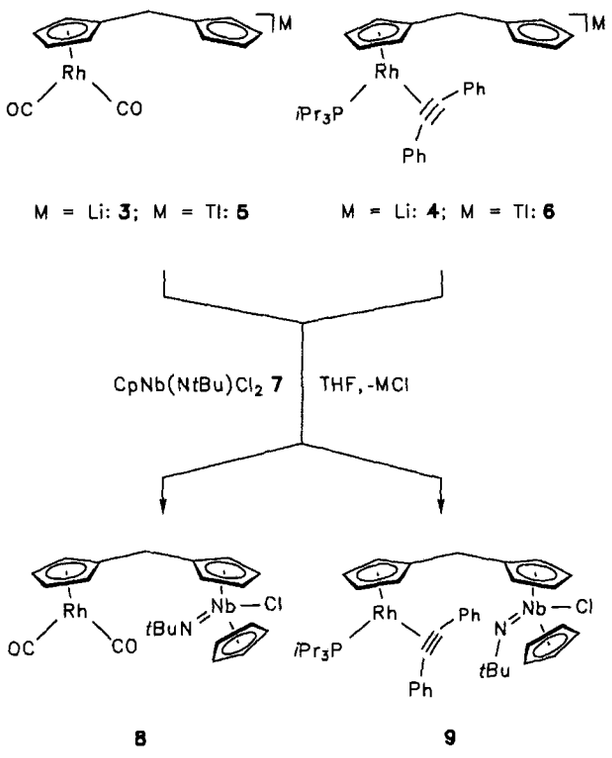
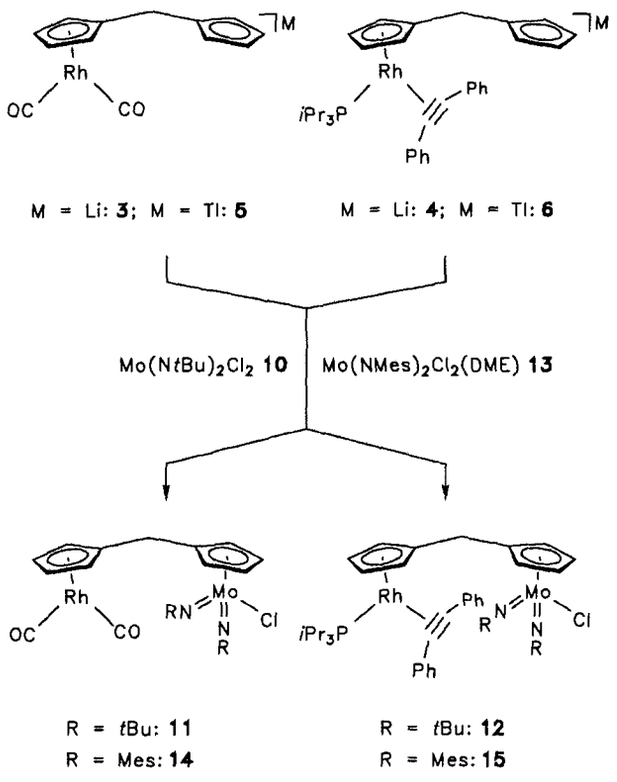
Scheme 1



Scheme 2



the two compounds. The most typical features of the ^{1}H- and ^{13}C-NMR spectra are the appearance of two sets of signals for each coordinated C_5H_4 unit with chemical shifts comparable to those of the well-known mononuclear $[(\eta^5\text{-}C_5H_5)Mo(NR)_2Cl]$ derivatives[8].

With regard to the proposed studies on the reactivity of the binuclear compounds, we were also interested in the synthesis of complexes containing an aryl instead of an alkyl substituent at the nitrogen atom of the imido ligand. We therefore investigated the reaction of the *N*-mesitylimido complex $[Mo(NMes)_2Cl_2(DME)]$ (**13**) with one equivalent of **3**–**6**. After removal of the solvent and separation of the reaction products, we were able to isolate the desired heterodinuclear complexes $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{Mo(NMes)_2Cl\}]$ (**14**) and $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(P\mathit{i}Pr_3)\}\{Mo(NMes)_2Cl\}]$ (**15**) as a red oil (**14**) or red solid (**15**) in moderate to good yields (Scheme 2).

Preparation of Mononuclear Nb and Mo Compounds

Treatment of solutions of the dichlorometal derivatives **7**, **10** and **13** in THF with the lithium or thallium salts $[(C_5H_5CH_2C_5H_4)M]$ (**16**, **17**) leads to the formation of the expected mononuclear complexes $[(C_5H_5CH_2C_5H_4)(C_5H_5)Nb(N\mathit{t}Bu)Cl]$ (**18**), $[(C_5H_5CH_2C_5H_4)Mo(N\mathit{t}Bu)_2Cl]$ (**19**) and $[(C_5H_5CH_2C_5H_4)Mo(NMes)_2Cl]$ (**20**) (Scheme 3). These are yellow or red oily substances which are soluble in all common organic solvents and are only slightly air-sensitive. The composition has been confirmed by elemental analysis and for **19** also by mass spectrometry.

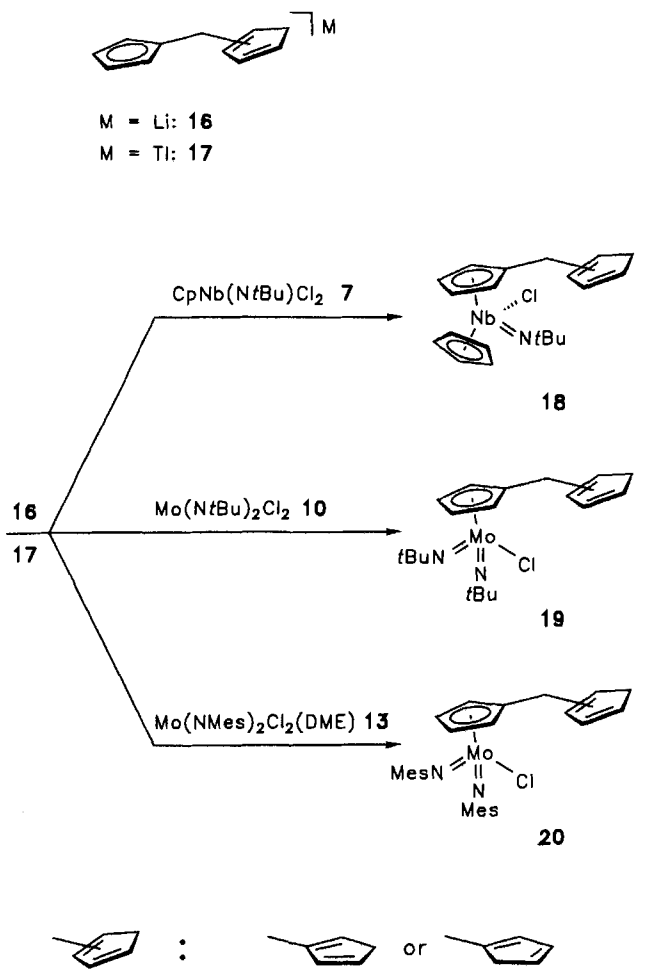
The NMR spectra for compounds **18**–**20**, for most of the protons and carbon atoms, display two sets of signals. Therefore, we assume that the uncoordinated dangling C_5H_5 ring is linked either at C-2 or C-3 to the methylene bridge and thus a mixture of two out of three possible isomers, similar to that found for the dicarbonyl compounds $[(C_5H_5CH_2C_5H_4)M(CO)_2]$ (M = Co, Rh, Ir), has been obtained[6]. The assignment for the ^{13}C resonances of the C_5H_4 ring carbon atoms follows the rule proposed by Coville et al.[9]; the *ipso*-C is less shielded than C-2 and C-5 and these are less so than C-3 and C-4.

Conclusion

The heterodinuclear complexes described in this work are, to the best of our knowledge, the first compounds in which a nucleophilic rhodium center and an electrophilic niobium or molybdenum center with additional imido ligands are held together in close proximity by a bridging ligand. Currently we are investigating the reactivity of these compounds towards nucleophilic and electrophilic reagents. The final goal is to perform a coupling reaction of the carbonyl or alkyne ligand bonded to rhodium with the imido ligand bonded to the electron-poor center. The mononuclear compounds **18**–**20** with a dangling (C_5H_4R) ligand are promising precursors for the preparation of mixed-valent heterobimetallics *with* or *without* an additional metal–metal bond.

This work was supported by the *Deutsche Forschungsgemeinschaft* (SFB 347) and the *Fonds der Chemischen Industrie*. We also thank the *Degussa AG* for generous gifts of chemicals, Mrs. *U. Neu-*

Scheme 3



mann, Mrs. *R. Schedl* and Mr. *C. P. Kneis* for elemental analyses, Dr. *G. Lange* and Mr. *R. Dadrich* for recording the mass spectra and Dr. *U. Radius* for helpful discussions.

Experimental

All operations were carried out under argon using the Schlenk-tube technique. Solvents were dried according to standard procedures and degassed with argon. The starting materials **1**–**4**[6,7], **7**[10], **10**[11], **13**[12], **16**[6] and $[(C_5H_5)_2CH_2]$[13] were prepared by published procedures; TlOEt was obtained commercially and was not further purified. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400; vt = virtual triplet, $N = {}^3J(PH) + {}^5J(PH)$. – MS: Varian MAT CH7.

Preparation of $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}Tl]$ (**5**): A solution of 197 mg (0.65 mmol) of **1** in 20 ml of ether was treated at 0 °C with 163 mg (0.65 mmol) of TlOEt. The reaction mixture was stirred for 1 h, the resulting yellow precipitate was filtered off, and repeatedly washed with pentane and dried in vacuo; yield 315 mg (96%).

Preparation of $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(PiPr_3)\}Tl]$ (**6**): A procedure analogous to that for **5** was employed, using 211 mg (0.36 mmol) of **2** and 90 mg (0.36 mmol) of TlOEt as starting materials; yellow powder; yield 278 mg (98%).

Preparation of $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{(C_5H_5)Nb(NtBu)Cl\}]$ (**8**): (a) A solution of 301 mg (1.00 mmol) of **7** in 15 ml of THF was treated at −78 °C with a solution of 308 mg (1.00 mmol) of **3** in 15 ml of THF. The yellow-brown reaction mixture was slowly warmed to room temperature and stirred for 3 h. It was then heated to 50 °C and stirred for 1 h. After cooling to 25 °C, the solvent was removed in vacuo and the residue was extracted with 20 ml of hexane. The extract was filtered through celite, the solvent was removed, and a yellow oil was obtained; yield 425 mg (76%). (b) A solution of 289 mg (0.96 mmol) of **7** in 20 ml of THF was treated at 0 °C with a suspension of 497 mg (0.96 mmol) of **5** in 15 ml of THF and then warmed to room temperature. The reaction mixture was stirred at room temperature for 24 h and then filtered with celite. The yellow filtrate was brought to dryness in vacuo and the residue was extracted three times with 10 ml of hexane. The extracts were combined, and after removal of the solvent, a yellow oil was obtained; yield 472 mg (87%). – IR (hexane): $\tilde{\nu}$ = 2040, 1979 cm^{-1} [ν(C≡O)], 1244 [ν(Nb=N–C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 6.03 (m, 2H, C_5H_4Nb), 5.87 (s, 5H, C_5H_5), 5.78 (m, 2H, C_5H_4Nb), 5.18 (vt, N = 4.0 Hz, 2H, C_5H_4Rh), 4.81 (m, 2H, C_5H_4Rh), 3.74 (br. s, 2H, CH_2), 0.95 (s, 9H, $C(CH_3)_3$). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 191.80 (d, J(RhC) = 84.8 Hz, C≡O), 132.73 (s, *ipso*-carbon of C_5H_4Nb), 111.79 (s, C-2 and -5 of C_5H_4Nb), 111.38 (s, C_5H_5), 110.81 (s, C-3 and -4 of C_5H_4Nb), 107.25 (d, J(RhC) = 4.1 Hz, *ipso*-carbon of C_5H_4Rh), 88.92 (d, J(RhC) = 3.1 Hz, C-2 and -5 of C_5H_4Rh), 86.13 (br. s, C-3 and -4 of C_5H_4Rh), 69.64 (s, $C(CH_3)_3$), 31.14 (s, CH_2), 29.80 (s, $C(CH_3)_3$). – $C_{22}H_{24}ClNNbO_2Rh$ (565.7): calcd. C 46.71, H 4.28, N 2.48; found C 46.48, H 4.23, N 2.40.

Preparation of $[\{CH_2(C_5H_4)_2\}\{Rh(PhC{\equiv}CPh)(PiPr_3)\}\{(C_5H_5)Nb(NtBu)Cl\}]$ (**9**): (a) A procedure analogous to that for **8** (a) was employed, using 129 mg (0.43 mmol) of **7** and 254 mg (0.43 mmol) of **4** as starting materials; yellow oil; yield 168 mg (46%). – (b) A procedure analogous to that for **8** (b) was employed, using 243 mg (0.81 mmol) of **7** and 638 mg (0.81 mmol) of **6** as starting materials; yellow oil; yield 543 mg (79%). – IR (hexane): $\tilde{\nu}$ = 1814 cm^{-1} [ν(C≡C)], 1248 [ν(Nb=N–C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 8.08 (m, 4H, C_6H_5), 7.33 (m, 6H, C_6H_5), 5.90 (m, 2H, C_5H_4Nb), 5.78 (s, 5H, C_5H_5), 5.63 (m, 2H, C_5H_4Nb), 5.28 (m, 2H, C_5H_4Rh), 5.08 (vt, N = 3.6 Hz, 2H, C_5H_4Rh), 3.40 (br. s, 2H, CH_2), 1.63 (m, 3H, $PCHCH_3$), 0.94 (dd, J(PH) = 12.8, J(HH) = 7.2 Hz, 18H, $PCHCH_3$), 0.90 (s, 9H, $C(CH_3)_3$). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 133.73 (s, *ipso*-carbon of C_6H_5), 131.98, 131.47 and 128.22 (each s, C_6H_5 and *ipso*-carbon of C_5H_4Nb), 126.04 (s, C-4 of C_6H_5), 111.50 (s, C-2 and -5 of C_5H_4Nb), 111.36 (s, C_5H_5), 109.01 (s, C-3 and -4 of C_5H_4Nb), 104.59 (dd, J(RhC) = 12.1, J(PC) = 3.6 Hz, *ipso*-carbon of C_5H_4Rh), 96.02 (dd, J(RhC) = 18.2, J(PC) = 5.0 Hz) and 95.86 (dd, J(RhC) = 18.0, J(PC) = 5.2 Hz, C≡C), 87.90 (m, C-2 and -5 of C_5H_4Rh), 82.60 (m, C-3 and -4 of C_5H_4Rh), 69.49 (s, $C(CH_3)_3$), 30.06 (s, CH_2), 29.97 (s, $C(CH_3)_3$), 26.13 (d, J(PC) = 21.6 Hz, $PCHCH_3$), 19.95 (s, $PCHCH_3$). – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 73.09 (d, J(RhP) = 200.7 Hz). – $C_{43}H_{55}ClNNbPRh$ (848.2): calcd. C 60.89, H 6.54, N 1.65, Rh 12.13; found C 61.41, H 6.33, N 2.07, Rh 11.92.

Preparation of $[\{CH_2(C_5H_4)_2\}\{Rh(CO)_2\}\{Mo(NtBu)_2Cl\}]$ (**11**): (a) A procedure analogous to that for **8** (a) was employed, using 192 mg (0.62 mmol) of **10** and 191 mg (0.62 mmol) of **3** as starting materials; orange-red oil; yield 217 mg (61%). – (b) A procedure analogous to that for **8** (b) was employed, using 253 mg (0.82 mmol) of **10** and 414 mg (0.82 mmol) of **5** as starting materials; orange-red oil; yield 344 mg (83%). – IR (hexane): $\tilde{\nu}$ = 2040, 1980 cm^{-1} [ν(C≡O)], 1254, 1220 [ν(Mo=N–C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 6.28 (m, 2H, C_5H_4Mo), 6.21 (m, 2H, C_5H_4Mo), 5.14 (vt, N = 4.1 Hz, 2H, C_5H_4Rh), 4.83 (m, 2H, C_5H_4Rh), 3.46 (br. s, 2H, CH_2), 1.27 (s, 18H, $C(CH_3)_3$). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 192.69 (d, J(RhC) = 84.8 Hz, C≡O), 133.88 (s, *ipso*-

carbon of C_5H_4Mo), 111.14 (d, J(RhC) = 4.4 Hz, *ipso*-carbon of C_5H_4Rh), 108.76 (s, C-2 and -5 of C_5H_4Mo), 107.50 (s, C-3 and -4 of C_5H_4Mo), 88.63 (d, J(RhC) = 3.1 Hz, C-2 and -5 of C_5H_4Rh), 86.16 (d, J(RhC) = 3.9 Hz, C-3 and -4 of C_5H_4Rh), 70.89 (s, $C(CH_3)_3$), 30.47 (s, CH_2), 30.16 (s, $C(CH_3)_3$). – $C_{21}H_{28}ClMoN_2O_2Rh$ (576.0): calcd. C 43.75, H 4.91, N 4.87; found C 43.81, H 4.97, N 4.63.

Preparation of [{CH$_2$(C$_5$H$_4$)$_2$}{Rh(PhC≡CPh)(PiPr$_3$)}{Mo(NtBu)$_2$Cl}] (**12**): (a) A solution of 118 mg (0.38 mmol) of **10** in 10 ml of ether was treated dropwise at −78 °C with a solution of 224 mg (0.38 mmol) of **4** in 15 ml of THF. The solution was warmed to room temperature over 2 h and stirred for 1 h further. It was then filtered with celite and the solvent removed in vacuo. The residue was extracted three times with 10 ml hexane each, and after the extracts were combined and concentrated in vacuo to approximately 1 ml, the solution was chromatographed on Al_2O_3 (activity grade V, length of column 7 cm) with hexane. The red fraction was separated and the solvent removed in vacuo to yield 222 mg (68%) of a red oil. – (b) A solution of 239 mg (0.76 mmol) of **10** in 15 ml of THF was treated at 0 °C with a suspension of 599 mg (0.76 mmol) of **6** in 15 ml of THF. The reaction mixture was warmed to room temperature and stirred for 24 h. The resulting suspension was filtered with celite and the filtrate evaporated in vacuo. The residue was extracted three times with 10 ml of hexane each and the extracts were treated as described for (a); red oil; yield 548 mg (84%). – IR (hexane): $\tilde{\nu}$ = 1816 cm^{-1} [ν(C≡C)], 1256, 1220 [ν(Mo=N−C)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 8.10 (m, 4H, C_6H_5), 7.24 (m, 6H, C_6H_5), 6.31 (m, 2H, C_5H_4Mo), 6.19 (m, 2H, C_5H_4Mo), 5.56 (m, 2H, C_5H_4Rh), 5.27 (vt, N = 4.0 Hz, 2H, C_5H_4Rh), 3.14 (br. s, 2H, CH_2), 1.61 (m, 3H, PC*H*CH$_3$), 1.31 (s, 18H, $C(CH_3)_3$), 0.87 (dd, J(PH) = 13.2, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 133.83, 132.97 (each s, *ipso*-carbon of C_6H_5 and C_5H_4Mo), 131.98, 131.87 and 128.82 (each s, C_6H_5), 125.81 (s, C-4 of C_6H_5), 108.93 (s, C-2 and -5 of C_5H_4Mo), 107.96 (s, C-3 and -4 of C_5H_4Mo), 105.16 (dd, J(RhC) = 12.4, J(PC) = 2.9 Hz, *ipso*-carbon of C_5H_4Rh), 96.33 (dd, J(RhC) = 19.8, J(PC) = 5.1 Hz) and 96.18 (dd, J(RhC) = 18.6, J(PC) = 5.1 Hz, C≡C), 87.62 (m, C-2 and -5 of C_5H_4Rh), 82.51 (d, J(RhC) = 3.7 Hz, C-3 and -4 of C_5H_4Rh), 69.71 (s, $C(CH_3)_3$), 30.31 (s, $C(CH_3)_3$), 29.81 (s, CH_2), 26.12 (d, J(PC) = 20.3 Hz, P*C*HCH$_3$), 19.92 (s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 73.15 (d, J(RhP) = 197.0 Hz). – $C_{42}H_{59}ClMoN_2PRh$ (858.2): calcd. C 58.73, H 6.93, N 3.26; found C 58.71, H 6.64, N 3.19.

Preparation of [{CH$_2$(C$_5$H$_4$)$_2$}{Rh(CO)$_2$}{Mo(NMes)$_2$Cl}] (**14**): (a) A procedure analogous to that for **8** (a) was employed, using 149 mg (0.48 mol) of **3** and 253 mg (0.48 mmol) of **13** as starting materials; red oil; yield 181 mg (54%). – (b) A procedure analogous to that for **8** (b) was employed, using 212 mg (0.42 mmol) of **5** and 220 mg (0.42 mmol) of **13** as starting materials; red oil; yield 214 mg (73%). – IR (hexane): $\tilde{\nu}$ = 2038, 1977 cm^{-1} [ν(C≡O)], 1322, 1280 [ν(Mo=N−C)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 6.72 (s, 4H, Mes-H), 6.47 (m, 2H, C_5H_4Mo), 6.41 (m, 2H, C_5H_4Mo), 5.19 (vt, N = 4.1 Hz, 2H, C_5H_4Rh), 4.92 (m, 2H, C_5H_4Rh), 3.57 (br. s, 2H, CH_2), 2.26 (s, 12H, *ortho*-CH_3), 2.01 (s, 6H, *para*-CH_3). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 192.01 (d, J(RhC) = 84.2 Hz, C≡O), 155.91 (s, C-1 of Mes), 135.09 (s, C-4 of Mes), 131.79 (s, *ipso*-carbon of C_5H_4Mo), 130.68 (s, C-2 of Mes), 127.98 (s, C-3 of Mes), 111.29 (s, C-2 and -5 of C_5H_4Mo), 107.43 (s, C-3 and -4 of C_5H_4Mo), 110.21 (d, J(RhC) = 4.3 Hz, *ipso*-carbon of C_5H_4Rh), 88.33 (d, J(RhC) = 3.2 Hz, C-2 and -5 of C_5H_4Rh), 86.34 (d, J(RhC) = 4.0 Hz, C-3 and -4 of C_5H_4Rh), 30.22 (s, CH_2), 21.03 (s, *para*-CH_3), 18.79 (s, *ortho*-CH_3). – $C_{31}H_{32}ClMoN_2O_2Rh$ (700.1): calcd. C 53.19, H 4.61, N 3.99; found C 53.22, H 4.47, N 4.08.

Preparation of [{CH$_2$(C$_5$H$_4$)$_2$}{Rh(PhC≡CPh)(PiPr$_3$)}{Mo(NMes)$_2$Cl}] (**15**): (a) A solution of 325 mg (0.55 mmol) of **4** in 20 ml of THF was added dropwise at −78 °C to a solution of 289 mg (0.55 mmol) of **13** in 15 ml of THF/ether (1:1). The reaction mixture was slowly warmed to room temperature and stirred for 6 h. The solvent was removed in vacuo, and the remaining dark brown residue was extracted three times with 10 ml of hexane (50 °C) each. The extracts were combined, the solution was concentrated in vacuo until a precipitate appeared, and then stored at −78 °C for 24 h. A red solid was obtained, which was repeatedly washed with pentane (−30 °C) and dried in vacuo to yield 248 mg (46%). – (b) A solution of 344 mg (0.66 mmol) of **13** in 15 ml of THF was treated at 0 °C with a suspension of 520 mg (0.66 mmol) of **6** in 20 ml of THF. After the reaction mixture was warmed to room temperature, it was stirred for 48 h. The resulting suspension was filtered with celite and the solvent removed in vacuo. The residue was extracted three times with 10 ml of hexane (50 °C) each, and the extracts were worked up as described for (a) to yield 460 mg (71%) of a red microcrystalline solid; m.p. 76 °C (dec.). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1822 cm^{-1} [ν(C≡C)], 1320, 1278 [ν(Mo=N−C)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 8.10 (m, 4H, C_6H_5), 7.24 (m, 6H, C_6H_5), 6.77 (s, 4H, Mes-H), 6.43 (m, 2H, C_5H_4Mo), 6.38 (m, 2H, C_5H_4Mo), 5.48 (m, 2H, C_5H_4Rh), 5.29 (vt, N = 4.1 Hz, 2H, C_5H_4Rh), 3.34 (br. s, 2H, CH_2), 2.30 (s, 12H, *ortho*-CH_3), 2.03 (s, 6H, *para*-CH_3), 1.63 (m, 3H, PC*H*CH$_3$), 0.93 (dd, J(PH) = 13.0, J(HH) = 7.1 Hz, 18H, PCHC*H*$_3$). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 155.82 (s, C-1 of Mes), 135.29 (s, C-4 of Mes), 133.79 (s, *ipso*-carbon of C_6H_5), 132.42 (s, *ipso*-carbon of C_5H_4Mo), 131.93, 131.81 and 128.92 (each s, C_6H_5), 130.67 (s, C-2 of Mes), 127.88 (s, C-3 of Mes), 125.77 (s, C-4 of C_6H_5), 110.81 (s, C-2 and -5 of C_5H_4Mo), 107.23 (s, C-3 and -4 of C_5H_4Mo), 104.92 (dd, J(RhC) = 12.5, J(PC) = 3.0 Hz, *ipso*-carbon of C_5H_4Rh), 96.14 (dd, J(RhC) = 19.6, J(PC) = 5.0 Hz) and 96.01 (dd, J(RhC) = 18.6, J(PC) = 5.1 Hz, C≡C), 87.88 (m, C-2 and -5 of C_5H_4Rh), 82.94 (d, J(RhC) = 3.8 Hz, C-3 and -4 of C_5H_4Rh), 31.01 (s, CH_2), 26.01 (d, J(PC) = 20.0 Hz, P*C*HCH$_3$), 20.99 (s, *para*-CH_3), 19.80 (s, PCH*C*H$_3$), 18.86 (s, *ortho*-CH_3). – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 72.97 (d, J(RhP) = 199.0 Hz). – $C_{52}H_{63}ClMoN_2PRh$ (981.4): calcd. C 63.64, H 6.47, N 2.85; found C 63.29, H 6.38, N 2.64.

Preparation of [(C$_5$H$_5$CH$_2$C$_5$H$_4$)Tl] (**17**): A solution of 968 mg (6.72 mmol) of [$(C_5H_5)_2CH_2$] in 25 ml of ether was treated at 0 °C with 627 mg (2.50 mmol) of TlOEt. The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting yellow precipitate was filtered, repeatedly washed with pentane and dried in vacuo to yield 816 mg (94%).

Preparation of [(C$_5$H$_5$CH$_2$C$_5$H$_4$)(C$_5$H$_5$)Nb(NtBu)Cl] (**18**): (a) A solution of 304 mg (1.01 mmol) of **7** in 20 ml of THF was treated at −78 °C with a solution of 158 mg (1.05 mmol) of freshly prepared **16** in 10 ml of THF. After the solution was warmed to room temperature it was stirred for 2 h and then heated to 40 °C. After stirring for 1 h it was cooled to room temperature. The solvent was removed in vacuo, the residue was extracted with 20 ml of hexane, and the extract was filtered with celite. The solvent was removed in vacuo to give 180 mg (44%) of a yellow oil. – (b) A solution of 264 mg (0.88 mmol) of **7** in 25 ml of THF was treated at 0 °C with a suspension of 313 mg (0.90 mmol) of **17** in 20 ml of THF. The reaction mixture was warmed to room temperature and stirred for 48 h. The solvent was removed in vacuo and the residue was worked up as described for (a); yellow oil; yield 232 mg (65%). –

IR (hexane): $\tilde{\nu}$ = 1248 cm^{-1} [ν(Nb=N−C)]. − ^1H NMR (C_6D_6, 400 MHz): δ = 6.51, 6.41, 6.34, 6.27, 6.18, 5.96 (each m, 3H, olefin protons of C_5H_5), 5.84 (s, 5H, C_5H_5Nb), 5.81 (m, 2H, C_5H_4Nb), 5.73 (m, 2H, C_5H_4Nb), 3.55, 3.50 (each br. s, 2H, CH_2), 2.75, 2.72 (each br. s, 2H, CH_2 of C_5H_5), 0.97, 0.95 (each s, 9H, $C(CH_3)_3$). − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 146.24, 145.49, (each s, *ipso*-carbon of C_5H_5), 135.36 (s, *ipso*-carbon of C_5H_4Nb), 134.41, 134.13, 132.18, 131.36, 128.94, 127.81 (each s, sp^2-carbons of C_5H_5), 111.93 (s, C-2 and C-5 of C_5H_4Nb), 111.33 (s, C_5H_5Nb), 110.79 (s, C-3 and -4 of C_5H_4Nb), 67.79, 67.72 (each s, $C(CH_3)_3$), 43.60, 41.33 (each s, CH_2 of C_5H_5), 31.06, 30.92 (each s, CH_2), 30.03, 29.88 (each s, $C(CH_3)_3$). − $C_{20}H_{25}ClNNb$ (407.8): calcd. C 58.91, H 6.18, N 3.43; found C 58.76, H 6.14, N 3.28.

Preparation of [($C_5H_5CH_2C_5H_4$)Mo(NtBu)$_2$Cl] (**19**): (a) To a solution of 605 mg (1.96 mmol) of **10** in 20 ml of THF a solution of 296 mg (1.97 mmol) of **16** in 15 ml of THF was added at −78 °C. The solution was warmed to room temperature and stirred for 4 h. The solvent was removed in vacuo, the residue was extracted three times with 10 ml of hexane each, and the combined extracts were filtered with celite. After the filtrate was concentrated approximately to 1 ml, it was chromatographed on Al_2O_3 (activity grade V, length of column 6 cm). With hexane, a red fraction was obtained, which, after removal of the solvent, yielded 416 mg (51%) of a red oil. − (b) A suspension of 417 mg (1.20 mmol) of **17** in 30 ml of THF was added to a solution of 372 mg (1.20 mmol) of **10** in 30 ml of THF at 0 °C. After the reaction mixture was warmed to room temperature and stirred for 48 h, the solvent was removed in vacuo and the residue extracted three times with 15 ml of hexane each. The extracts were combined and filtered with celite. The solvent was removed in vacuo to give 416 mg (83%) of a red oil. − IR (hexane): $\tilde{\nu}$ = 1258, 1220 cm^{-1} [ν(Mo=N−Cl)]. − ^1H NMR (C_6D_6, 400 MHz): δ = 6.51, 6.42, 6.33, 6.19, 5.99, 5.87 (each m, 3H, olefin protons of C_5H_5), 6.36 (m, 2H, C_5H_4Mo), 6.09 (m, 2H, C_5H_4Mo), 3.42 (m, 2H, CH_2), 2.86 (m, 2H, CH_2 of C_5H_5), 1.15, 1.12 (each s, 18H, $C(CH_3)_3$). − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 148.14, 145.89 (each s, *ipso*-carbon of C_5H_5), 133.26 (s, *ipso*-carbon of C_5H_4Mo), 135.14, 133.78, 132.70, 131.16, 128.29, 127.08 (each s, sp^2-carbons of C_5H_5), 108.14 (s, C-2 and -5 of C_5H_4Mo), 106.23 (s, C-3 and -4 of C_5H_4Mo), 68.22, 67.76 (each s, $C(CH_3)_3$), 43.50, 41.27 (each s, CH_2 of C_5H_5), 32.02, 31.70 (each s, $C(CH_3)_3$), 30.97 (br. s, CH_2). − $C_{19}H_{29}ClMoN_2$ (417.6): calcd. C 54.75, H 7.00, N 6.71; found C 54.16, H 6.68, N 6.39; mol. mass 418 (MS).

Preparation of [($C_5H_5CH_2C_5H_4$)Mo(NMes)$_2$Cl] (**20**): (a) To a solution of 1.47 g (2.80 mmol) of **13** in 25 ml of THF a solution of 421 mg (2.80 mmol) of **16** in 25 ml of THF was added at −78 °C. The solution was slowly warmed to room temperature and stirred for 18 h. The solvent was removed, the residue was extracted three times with 20 ml of hexane each, and the combined extracts were filtered with celite. After the filtrate was concentrated in vacuo to approximately 1 ml, it was chromatographed on Al_2O_3 (activity grade V, length of column 10 cm). With toluene, a red fraction was obtained, which, after removal of the solvent, yielded 1.17 g (77%) of a red oil. − (b) A solution of 420 mg (0.80 mmol) of **13** in 25 ml of THF was treated at 0 °C with a suspension of 278 mg (0.80 mmol) of **17** in 20 ml of THF. The reaction mixture was warmed to room temperature and stirred for 48 h. After removal of the solvent the residue was worked up as described for (a) to yield 373 mg (86%) of a red oil. − IR (hexane): $\tilde{\nu}$ = 1324, 1282 cm^{-1} [ν(Mo=N−C)]. − ^1H NMR (C_6D_6, 200 MHz): δ = 6.69, 6.60 (each s, 4H, Mes-H), 6.49, 6.29, 6.18, 5.93, 5.82, 5.77 (each m, 3H, olefin protons of C_5H_5), 6.44 (m, 2H, C_5H_4Mo), 6.40 (m, 2H, C_5H_4Mo), 3.35 (br. s, 2H, CH_2), 2.76, 2.70 (each s, 2H, CH_2 of C_5H_5), 2.30, 2.18 (each s, 12H, *ortho*-CH_3), 2.07, 1.91 (each s, 6H, *para*-CH_3). − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 155.63 (s, C-1 of Mes), 148.20, 147.31 (each s, *ipso*-carbon of C_5H_5), 135.09, 135.01 (each s, C-4 of Mes), 133.26 (s, *ipso*-carbon of C_5H_4Mo), 134.76, 134.23, 133.72, 132.79, 131.16, 130.99, 129.17, 128.14, 127.06 (each s, sp^2-carbons of C_5H_5, C-2 and C-3 of Mes), 110.16 (s, C-2 and -5 of C_5H_4Mo), 105.93 (s, C-3 and -4 of C_5H_4Mo), 43.47, 41.41 (each s, CH_2 of C_5H_5), 30.93, 30.17 (each s, CH_2), 21.61, 21.01 (each s, *para*-CH_3), 19.17, 17.65 (each s, *ortho*-CH_3). − $C_{29}H_{33}ClMoN_2$ (542.1): calcd. C 64.19, H 6.15, N 5.18; found C 64.59, H 6.27, N 5.22.

☆ Dedicated to Prof. Dr. *Herbert Schumann* on the occasion of his 60th birthday.

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