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Chelate Complexes with Tripodal Triisocyanide Ligands: Synthesis and Crystal Structures of *fac*-$\{[N(CH_2CH_2CH_2O\text{-}3\text{-}CNC_6H_4)_3]W(CO)_3\}\cdot 0.5CH_2Cl_2$ and *fac*-$\{[N(CH_2CH_2CH_2O\text{-}2\text{-}CNC_6H_4)_3]W(CO)_3\cdot HCl\}\cdot 2.5CH_2Cl_2$

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The tripodal triisocyanide ligands tris[3-(3-isocyanophenoxy)propyl]amine (**4**, *m*-tarc), tris[3-(2-isocyanophenoxy)propyl]amine (**5**, *o*-tarc), and tris(3-isocyanopropyl)amine (**6**, talc) react with *fac*-$[(C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) to give the chelate complexes *fac*-$[(m\text{-tarc})W(CO)_3]$ (**7**), *fac*-$[(o\text{-tarc})M(CO)_3]$ [**8**; M = Cr (**a**), Mo (**b**), W (**c**)], and $[(\text{talc})W(CO)_3]$ (**9**), respectively. The molecular structures of **7** and **8c** were determined by X-ray structure analysis, showing that indeed chelate complexes had formed. **7** crystallized with 0.5 molecules of CH_2Cl_2 in the crystal lattice. The central nitrogen atom adopts the "in" configuration. **8c** crystallized as the hydrochloride with 2.5 molecules of CH_2Cl_2 in the crystal lattice. The protonated central nitrogen atom is in the "out" configuration. Crystal data: for **7**·$0.5CH_2Cl_2$, monoclinic, $C2/c$, a = 14.848 (3) Å, b = 26.016 (7) Å, c = 17.866 (5) Å, β = 101.56 (2)°, Z = 8, R = 0.0500, and R_w = 0.0399 for 3208 reflections [$I \geq 2\sigma(I)$]; for **8c**·HCl·$2.5CH_2Cl_2$, triclinic, $P\bar{1}$, a = 12.491 (4) Å, b = 13.414 (4) Å, c = 15.365 (2) Å, α = 114.73 (2)°, β = 105.39 (2)°, γ = 101.89 (2)°, Z = 2, R = 0.0410, and R_w = 0.0559 for 5052 reflections ($I \geq 3\sigma(I)$].

Introduction

Compared to the coordination chemistry of monodentate isocyanides, relatively little is known about the coordination chemistry of multidentate isocyanide ligands. Some aliphatic di-[1] and triisocyanide[2] ligands and their coordination chemistry have been reported. Various studies have shown that aliphatic diisocyanide ligands which contain less then seven methylene groups between the isocyanide functions are incapable of coordination to a single metal with both isocyanide groups.[1d,e] Consequently, only few examples of chelating aliphatic diisocyanide ligands are known. To our knowledge, only two reports of such ligands have appeared.[1d,e] A notable example of an aromatic chelating diisocyanide is the ligand DiNC,[3] $[CH_2O\text{-}2\text{-}CN\text{-}C_6H_4]_2$, which has been shown to form chelate complexes with a number of transition metals.[4] Recently, others[5] and we[6] described the synthesis and coordination chemistry of the tripodal triisocyanide ligand $H_3CC(CH_2NC)_3$. This ligand is capable of capping a triangular face in clusters like $Os_3(CO)_{12}$[5] or $Fe_3(CO)_{12}$.[6]

Table I. IR Data for *m*-tarc, *o*-tarc, talc, and Their Metal Complexes[a]

compd	ν(NC), cm^{-1} A_1	ν(NC), cm^{-1} E	ν(CO), cm^{-1} A_1	ν(CO), cm^{-1} E
m-tarc (**4**)	2113			
o-tarc (**5**)	2118			
talc (**6**)	2148			
fac-[(*m*-tarc)W(CO)$_3$ (**7**)	2118	2052	1950	1900
fac-[(o-tarc)Cr(CO)$_3$ (**8a**)	2140	2078	1940	1885
fac-[(o-tarc)Mo(CO)$_3$ (**8b**)	2138	2079	1940	1888
fac-[(o-tarc)W(CO)$_3$ (**8c**)	2137	2068	1933	1878
(talc)W(CO)$_3$ (**9**)	2160	2115	1932	1854

[a] All IR spectra were recorded in KBr.

Recent interest in isocyanide ligands is based on their application in nuclear medical diagnosis. Davison has shown[7] that monodentate isocyanide ligands from stable octahedral complexes of the type $[Tc(CNR)_6]^+$, which find use in the myocardial scintigraphy[8] owing to the superb radiophysical properties ($t_{1/2}$ = 6.02 h, E_γ = 140.6 keV) of the metastable isotope ^{99m}Tc. To obtain particularly stable isocyanide complexes, we have initiated a program to synthesize and evaluate tripodal, potentially chelating triisocyanide ligands. Recently we synthesized the first two examples of such ligands, talc and *o*-tarc (Figure 1) and reported in a preliminary study on their coordination chemistry with respect to chelate formation with transition metals[9] and ^{99m}Tc.[10] In this contribution we wish to report the synthesis of the new tripodal triisocyanide ligand *m*-tarc (**4**) (Figure 1) together with the crystal structures of the chelate complexes *fac*-$[(m\text{-tarc})W(CO)_3]\cdot 0.5CH_2Cl_2$ (**7**·$0.5CH_2Cl_2$) and *fac*-$[(o\text{-tarc})W(CO)_3]\cdot HCl\cdot 2.5CH_2Cl_2$ (**8c**·HCl·$2.5CH_2Cl_2$).

Results and Discussion

Synthesis of Ligands and Metal Complexes. The synthesis of ligand *m*-tarc (**4**) is shown in Scheme I. The ligand was synthesized by Williamson coupling of the potassium salt of *m*-nitrophenol with tris(3-chloro-

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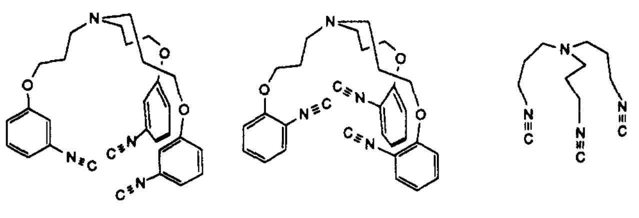


m-tarc, **4** *o*-tarc, **5** talc, **6**

Figure 1. Tripodal triisocyanide ligands.

propyl)amine,[11] followed by reduction of the three aromatic nitro groups with PtO_2/H_2 and subsequent formylation of the amino groups with acetic formic anhydride.[3] The three formamide groups of **3** were converted into isocyanide functions with diphosgene/NEt_3 according to the method of Meyr and Ugi.[12] The ligand is a colorless oil which is soluble in chlorinated hydrocarbons, THF, and diethyl ether. The preparation of *o*-tarc (**5**) is similar and has been described in ref 10. The ligand tacl (**6**) was prepared as described in ref 9a.

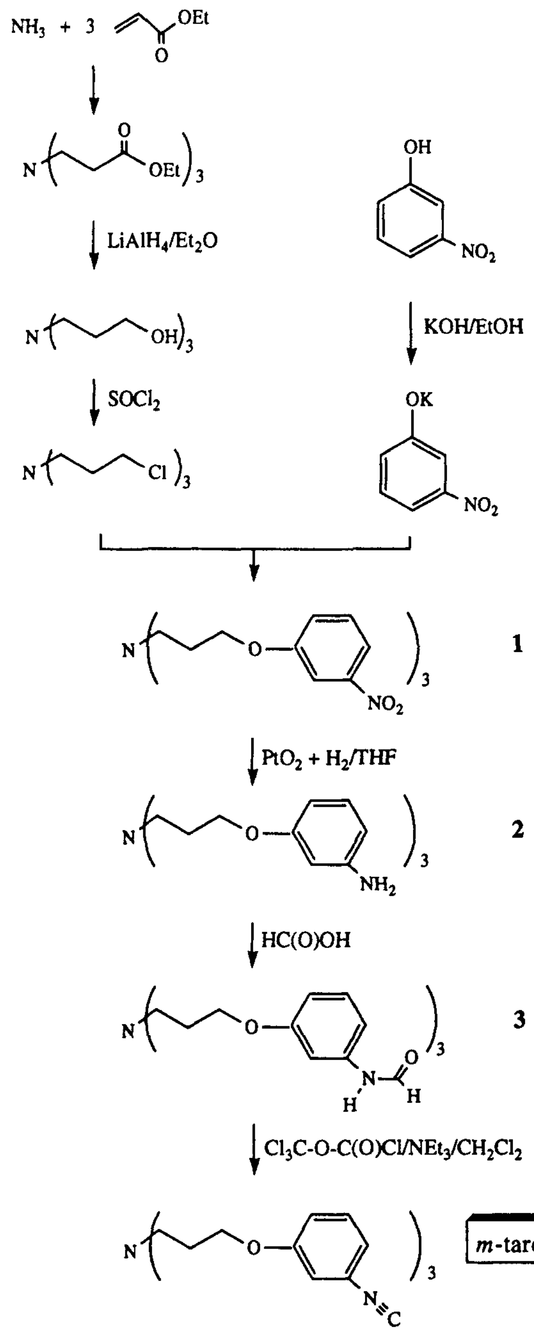
The ^{13}C NMR RNC resonances (in $CDCl_3$) for the two aromatic isocyanides appear at $\delta = 164.0$ ppm (*m*-tarc) and $\delta = 167.6$ (*o*-tarc) as broad singlets, while the isocyanide resonance for talc is observed as a triplet at $\delta = 156.5$ ppm ($^1J(^{13}C, ^{14}N) = 5.60$ Hz). ^{13}C, ^{14}N coupling has been observed for various isocyanides.[13]

The absorption in the IR spectrum shifts from $\nu = 2118$ cm^{-1} for *o*-tarc[9a] to $\nu = 2113$ cm^{-1} for *m*-tarc. Previous studies also have shown that the NC frequencies of aromatic isocyanides are constitution dependent.[12] Delocalization of electron density from the isocyanide group into the aromatic ring is facilitated by meta substitution of the ring as compared to ortho substitution. Therefore, the meta-substituted aromatic isocyanide should be a better π acceptor then *o*-tarc and both aromatic isocyanides are better π acceptors then talc (ν(NC) = 2148 cm^{-1}) (Table I).

Reaction of *m*-tarc, *o*-tarc, or talc with *fac*-$[(C_7H_8)M(CO)_3]$ (M = Cr, Mo, W)[14] in dichloromethane leads in good yield to the complexes *fac*-[(*m*-tarc)$W(CO)_3$] (**7**), *fac*-[(*o*-tarc)$M(CO)_3$] [**8**; M = Cr (**a**), Mo (**b**), W (**c**)], and [(talc)$W(CO)_3$] (**9**). **7** and **8a–c** were initially obtained as slightly yellow chloroform- and dichloromethane-soluble powders. **9** was insoluble in these solvents after it had precipitated in the course of the reaction from the reaction solution.

The IR spectra of the compounds showed local C_{3v} symmetry (Table I), indicating that chelates could have formed. No significant shift in the wavenumbers occurred in the series **8a–c** for the CO and NC vibrations. However, comparison of the data for **7** and **8c** showed significant differences. The CO absorptions for **7** appear at significantly higher wavenumbers than in **8c**, while the NC absorptions for **7** are observed approximately 15 wavenumbers lower than for **8c**. As indicated by the IR spectra of the free ligands, *m*-tarc is a better π acceptor and a weaker σ donor than *o*-tarc. Both aromatic isocyanides are, as expected, better π acceptors and weaker σ donors than talc in **9**.

Scheme I



The IR data for **9** are in good agreement with the values for the triisocyanide complex *fac*-[(*t*-BuNC)$_3W(CO)_3$] [ν(NC) 2161 (A_1), 2114 cm^{-1} (E); ν(CO) 1932 (A_1), 1856 cm^{-1} (E)].[15] The IR absorptions of the complexes containing *o*-tarc are comparable to the values observed for complexes of the type *fac*-[(aromatic isocyanide)$_3M(CO)_3$] (M = Cr, Mo[16,17]). However, in these studies only para-substituted aromatic isocyanides were used. As indicated earlier, meta substitution of an aromatic isocyanide induces better π-acceptor and weaker σ-donor properties. A comparison of **7** with another complex of the type *fac*-[(meta-substituted aromatic isocyanide)$_3W(CO)_3$] is currently not possible, since we are not aware of another compound of this type.

7 is stable in dichloromethane and can be recrystallized from this solvent. The initially slightly dichloromethane-soluble compounds **8a–c** react (upon recrystal-

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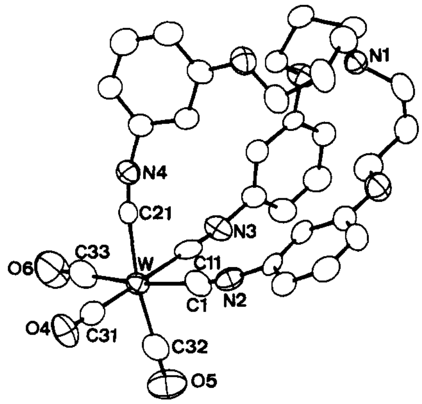

Figure 2. Molecular structure of the complex 7 in 7·$0.5CH_2Cl_2$.

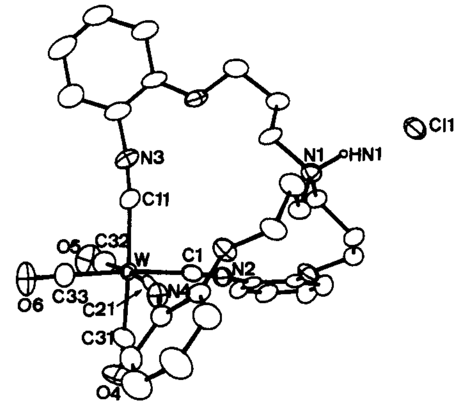

Figure 3. Molecular structure of the complex 8c·HCl in 8c·HCl·$2.5CH_2Cl_2$.

lization) within a few hours with dichloromethane or impurities in this solvent (HCl) giving dichloromethane-insoluble products, which showed unsatisfactory CHN analyses but almost unchanged IR spectra. Therefore, only 7 was characterized NMR spectroscopically. The ^{13}C NMR spectrum of 7 (in CD_2Cl_2) showed the resonance for the isocyanide carbon atom only slightly shifted from the value of the free ligand at $\delta = 161.6$ ppm and the CO resonance at $\delta = 204.4$ ppm. These values are in good agreement with the ^{13}C NMR data for *fac*-[(*p*-tolNC)$_3$W(CO)$_3$] (δ(NC) = 160 ppm, δ(CO) = 203 ppm).[18]

To establish the complexes undoubtedly as chelates, various attempts to obtain single crystals were made. 7 and 8c gave satisfactory single crystals from a dichloromethane solution. The crystals of 7 were still soluble in CH_2Cl_2, while the solubility of 8c decreased with each recrystallization, and crystals of this compound did not redissolved in dichloromethane. Furthermore, the CHN analyses of recrystallized, CH_2Cl_2-insoluble 8c showed deviations from the theoretical values.

Crystal Structures of 7 and 8c. The structure analyses showed that both 7 and 8c crystallized with dichloromethane in the crystal lattice (0.5 molecules for each molecule of 7 and 2.5 molecules for each molecule of 8c). These solvent molecules can be removed in vacuo, giving the solvent-free derivatives. Furthermore, 8c crystallized as hydrochloride 8c·HCl by reaction with the solvent or impurities in the solvent (HCl). This explains the unsatisfactory CHN analyses and insolubility for recrystallized, solvent-free 8c. Selected bond distances and angles for the two compounds are listed in Table II. The numbering scheme used in this table is explained in Figures 2 and 3, which show plots of 7 and 8c·HCl.

Table II. Selected Bond Distances (Å) and Angles (deg) for 7•$0.5CH_2Cl_2$ and 8c•HCl•$2.5CH_2Cl_2$

	7·$0.5CH_2Cl_2$	8c·HCl·$2.5CH_2Cl_2$
W–C1	2.120 (11)	2.109 (6)
W–C11	2.087 (11)	2.107 (6)
W–C21	2.087 (11)	2.126 (6)
W–C31	2.010 (11)	1.988 (5)
W–C32	1.984 (13)	1.970 (6)
W–C33	1.989 (12)	1.995 (6)
C1–N2	1.136 (14)	1.168 (7)
C11–N3	1.172 (13)	1.169 (7)
C21–N4	1.168 (14)	1.165 (7)
C31–O4	1.176 (13)	1.161 (6)
C32–O5	1.174 (16)	1.178 (7)
C33–O6	1.158 (14)	1.161 (7)
N1–HN1		0.74 (7)
HN1–Cl1		2.27 (8)
C1–W–C11	83.6 (4)	93.6 (2)
C1–W–C21	82.7 (4)	98.6 (2)
C1–W–C31	92.3 (4)	87.7 (2)
C1–W–C32	93.2 (4)	87.6 (2)
C1–W–C33	172.5 (5)	174.9 (2)
C11–W–C21	82.4 (4)	93.3 (2)
C11–W–C31	175.1 (4)	175.4 (2)
C11–W–C32	89.7 (4)	88.6 (2)
C11–W–C33	92.2 (4)	91.1 (2)
C21–W–C31	94.4 (4)	90.8 (2)
C21–W–C32	171.4 (4)	173.3 (2)
C21–W–C33	90.6 (4)	83.3 (2)
C31–W–C32	93.3 (4)	87.1 (3)
C31–W–C33	91.5 (4)	87.5 (2)
C32–W–C33	93.0 (5)	90.4 (2)
W–C1–N2	174.3 (11)	173.1 (4)
W–C11–N3	174.2 (8)	174.3 (4)
W–C21–N4	172.5 (8)	171.2 (4)
W–C31–O4	178.0 (8)	176.6 (5)
W–C32–O5	177.6 (9)	176.4 (5)
W–C33–O6	178.1 (11)	177.6 (5)
C10–N1–C20	111.6 (7)	110.5 (4)
C10–N1–C30	112.2 (8)	110.8 (4)
C20–N1–C30	111.8 (8)	110.4 (4)
C1–N2–C2	163.8 (10)	169.6 (5)
C11–N3–C12	168.0 (9)	172.4 (6)
C21–N4–C22	165.6 (10)	173.1 (4)

The structure analyses prove that *m*-tarc and *o*-tarc are indeed capable of forming chelate complexes with transition metals in low oxidation states. No polymers are detected in the preparation of 7. However, in the synthesis of 8c a dimeric side product, *fac,fac*-[(*o*-tarc)W(CO)$_3$·HCl]$_2$·$2CH_2Cl_2$, can be isolated in low yield.[9b] The W atoms in both 7 and 8c·HCl are coordinated in a slightly distorted, facial octahedral fashion by three isocyanide and three carbonyl carbon atoms. Three 18-membered chelate rings are formed in 8c, while these rings contain 20 atoms each in 7. These chelate rings belong to the largest observed in organometallic compounds. In both derivatives the W–C–O angles are closer to linearity than the W–C–N angles. The observed W–CN distances for both complexes are identical within experimental error. To our knowledge, no complex of the type *fac*-[(RNC)$_3$W(CO)$_3$] has been characterized crystallographically until now. However, the W–CO and W–CN distances in 7 and 8c are very similar to equivalent distances in compounds of the type (RNC)W(CO)$_5$ [range d(W–CO) = 1.98 (1)–2.08 (1) Å, range d(W–CN) = 2.06 (1)–2.10 (1)Å],[19] (CO)$_4$W[C(OCH$_3$)(C$_5$H$_5$)](CNC$_6$H$_4$-*p*-CH$_3$) [range d(W–CO) = 1.950 (19)–2.043 (17) Å, d(W–CN) = 2.096 (19) Å],[20] and

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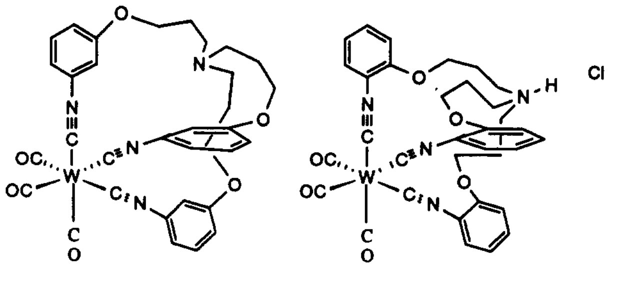

(*m*-tarc)W(CO)$_3$, **7**: "in" (*o*-tarc)W(CO)$_3$·HCl, **8c**·HCl: "out"

Figure 4. Schematic representations of the complexes **7** and **8c**·HCl.

[(CO)$_4$(PR$_3$)WCNC$_6$H$_4$NCW(CO)$_4$(PR$_3$)] [range *d*(W–CO) = 1.973 (15)–2.060 (18) Å, *d*(W–CN) = 2.065 (12) and 2.084 (11) Å][21] or even to the distances in the heptacoordinated W(II) complexes W(CO)$_2$(I)$_2$(*t*-C$_4$H$_9$NC)$_3$.[22] X-ray crystallography is obviously not capable of detecting the differences in the electronic structure of the aforementioned compounds via differences in the bond distances. This is also confirmed by a comparison of the W–CO and W–CN distances in **7** and **8c**. IR spectra clearly show that *m*-tarc in **7** is a far better π acceptor and a weaker σ donor than *o*-tarc in **8c**. However, no significant differences in the W–CO and W–CN distances between the two complexes are noticeable.

The most remarkable difference between **7** and **8c**·HCl is the configuration of the central nitrogen atom of the backbone of the ligand. In **7** this atom adopts the "in" configuration like in a number of metal complexes with tripodal ligands.[23] It is not protonated like the central nitrogen atom in the tricatechol complexes K$_3$[V(TRENCAM)][23c] or Na$_3$[Fe(bicapped TRENCAM)].[23b] Protonation of the central nitrogen atoms in the "in" configuration is geometrically possible and has been shown to exist in the tricatechol complex [HNEt$_3$][Ti(TRIPACE).[23a] The central nitrogen atom in **8c**·HCl is in the "out" configuration and protonated. The complex is actually a hydrochloride with a nonbonding HN1··Cl distance of 2.27 (8) Å. To our knowledge, this situation has not been described yet for a metal complex with a tripodal ligand. The ligand *o*-tarc, however, does not become protonated when dissolved in CH$_2$Cl$_2$. Only in the metal complex does protonation occur. The source of HCl is presently not known to us. Possible sources are HCl impurities in the dichloromethane or reaction of the central nitrogen atom under carbene formation with the solvent. In any case, coordination of *o*-tarc to a metal center leads to a stronger basicity of the central nitrogen, possibly because of hinderance of the inversion at the nitrogen atom. The chelate rings in **7** are slightly larger, which might allow for inversion at N1 and thus prevents protonation of this atom, which is geometrically possible and has been demonstrated for a tricatechol complex.[23a]

Conclusion

The ligands *o*-tarc and *m*-tarc are capable of forming chelate complexes with group VIb transition metals in low oxidation states. The bonding situation in these complexes is shown schematically in Figure 4. The unusually large size of the chelate rings (18 atoms in **8c**·HCl, 20 atoms in **7**) does not prevent chelate formation nor does it lead to polynuclear complexes or polymers. Presently we do not know the molecular structure of **9**. IR data show local C_{3v} symmetry which is consistent with both monomeric *fac*-[(talc)W(CO)$_3$] or its hydrochloride and polymeric [(talc)W(CO)$_3$]$_\infty$. The insolubility of **9** prevented further investigations. No chlorine was detected, which rules out the formation of a hydrochloride, which in turn would explain the poor solubility. Geometrically talc is able to form a chelate complex. However, the poor solubility in the absence of a hydrochloride points toward formation of a polymer.

The good solubility and stability of **7** makes this compound a superb starting material for reactions at the coordinated isocyanide groups. It appears possible to convert all three isocyanide groups into carbenes. Corresponding investigations are in progress.

Experimental Section

All operations were performed under dry argon by using Schlenk and vacuum techniques. All solvents were dried by standard methods and distilled prior to use. ^{1}H NMR spectra were recorded on a Bruker WP 80 instrument (80 MHz), and ^{13}C NMR spectra, on a Bruker WP 80 SY spectrometer (20.15 MHz). Infrared spectra were taken in KBr on a Perkin-Elmer 580 B instrument. The ligands *o*-tarc (**5**)[10] and talc (**6**)[9a] were prepared by literature methods.

Tris[3-(3-nitrophenoxy)propyl]amine (1). A 35.21-g (253-mmol) amount of 3-nitrophenol (Aldrich) was dissolved in 200 mL of absolute 2-propanol. A 14.16-g amount of KOH was dissolved in 100 mL of 2-propanol and added to the nitrophenol solution. Upon addition the red potassium 3-nitrophenolate precipitated. It redissolved if the solution was warmed to 50 °C, giving a dark red solution. To this solution was added 20.86 g (85 mmol) of tris(3-chloropropyl)amine[11] in 50 mL of 2-propanol. The reaction mixture was refluxed for 3 days and subsequently cooled to room temperature. A 200-mL volume of acetone was added to dissolve the oily precipitate which appeared upon cooling. Now the formed KCl was separated by filtration and washed with acetone. The combined organic solutions were concentrated giving **1** as yellow needles. These were washed with cold 2-propanol and dried in vacuo (26.53 g, 57%). ^{1}H NMR (CDCl$_3$): δ 7.86–7.00 (m, 12 H, Ar *H*), 4.00 (t, 6 H, C*H*$_2$O), 2.67 (t, 6 H, C*H*$_2$N), 1.96 (quint, 6 H, CH$_2$C*H*$_2$). ^{13}C{H} NMR (CDCl$_3$): δ 159.3, 148.9, 129.8, 120.9, 115.3, 108.6 (Ar *C*), 66.1 (CH$_2$O), 49.7 (CH$_2$N), 26.7 (*C*-H$_2$CH$_2$). Anal. Calcd for C$_{27}$H$_{30}$H$_4$O$_9$ (M$_r$ = 554.56): C, 58.48; H, 5.45; N, 10.10. Found: C, 57.0; H, 5.11; N, 10.41.

Tris[3-(3-aminophenoxy)propyl]amine (2). A 5.0-g (9-mmol) amount of **1** was dissolved in 100 mL of THF. To this solution was added 100 mg of Pd/C hydrogenation catalyst (10% Pd, Aldrich). The reaction mixture was stirred in an autoclave under H$_2$ (200 bar) for 12 h. Subsequently, the reaction mixture was filtered to separate the Pd catalyst. The THF was stripped in vacuo leaving **2** as yellow oil which turned dark in contact with air (3.9 g, 93%). ^{1}H NMR (CDCl$_3$): δ 7.14–5.93 (m, 12 H, Ar *H*), 3.91 (s, br, 6 H, Ar–N*H*$_2$), 3.61 (t, 6 H, C*H*$_2$O), 2.56 (t, 6 H, C*H*$_2$N), 1.82 (quint, 6 H, CH$_2$C*H*$_2$). ^{13}C{H} NMR (CDCl$_3$): δ 160.3, 147.7, 129.8, 107.0, 105.6, 105.1 (Ar *C*), 64.0 (*C*H$_2$O), 48.6 (*C*H$_2$N), 26.5 (*C*H$_2$CH$_2$). Satisfactory CHN analyses for **2** could note be obtained. Samples were hard to prepare, since the compound was oily and quite air sensitive.

Tris[3-(3-formamidophenoxy)propyl]amine (3). A 1.5-g (3.2-mmol) sample of the tetraamine **2** was dissolved in 50 mL of THF, and 1.0 g (11.0 mmol) of acetic formic anhydride was added. The reaction mixture was stirred at room temperature for 2 h. Then all volatile material was removed at a rotary evaporator. The resulting viscous oil was dissolved in 50 mL of dichloromethane. This solution was washed three times with 50 mL of aqueous Na$_2$CO$_3$ solution (10%) and dried with Na$_2$SO$_4$. The solvent was stripped from the resulting clear dichloromethane solution giving pure **3** as white powder (1.7 g, 96%). ^{1}H NMR

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(acetone-d_6): δ 9.25 (s, br, 3 H, N*H*CHO), 8.36 (s, 3 H, C*H*O), 7.33–6.50 (m, 12 H, Ar *H*), 3.90 (t, 6 H, C*H*$_2$O), 2.60 (t, 6 H, C*H*$_2$N), 1.85 (quint, 6 H, CH$_2$C*H*$_2$). Anal. Calcd for $C_{30}H_{36}N_4O_6$ (M_r = 548.64): C, 65.68; H, 6.61; N, 10.21. Found: C, 65.32; H, 6.58; N, 10.16.

Tris[3-(3-isocyanophenoxy)propyl]amine (4, *m*-tarc). A 1.46-g (2.7-mmol) amount of 3 in 50 mL of dichloromethane and 5 mL of triethylamine was mixed in a three-necked round-bottom flask equipped with argon inlet, a magnetic stirrer, thermometer, condenser, and rubber septum. The mixture was cooled to −78 °C, and 0.5 mL of diphosgene was added via the septum with a syringe (*Caution!* Disphosgene is toxic and may liberate phosgene in the course of the reaction; the reaction must be carried out in a well-ventilated fume hood). The brown solution was allowed to warm to room temperature and was stirred for an additional 12 h. The reaction mixture was then washed once with water (100 mL) and twice with an aqueous Na_2CO_3 solution (10%). The brown dichloromethane solution was then dried with Na_2SO_4, and all solvents were removed in vacuo. The resulting oil was purified chromatographically on Al_2O_3 (4% H_2O) with dichloromethane giving a colorless oil (430 mg, 33%). ^{1}H NMR (CDCl$_3$): δ 7.25–6.61 (m, 12 H, Ar *H*), 3.75 (t, 6 H, C*H*$_2$O), 2.51 (t, 6 H, C*H*$_2$N), 1.79 (quint, 6 H, CH$_2$C*H*$_2$). ^{13}C{H} NMR (CDCl$_3$): δ 164.0 (br, Ar–NC), 159.3, 130.1 (Ar *C*), 127.2 (br, Ar *C*–NC), 118.5, 115.5, 112.1 (Ar *C*), 65.6 (CH$_2$O), 49.5 (CH$_2$N), 26.6 (CH$_2$CH$_2$). Anal. Calcd for $C_{30}H_{30}N_4O_3$ (M_r = 494.60): C, 72.85; H, 6.11; N, 11.33. Found: C, 72.13; H, 6.18; N, 10.94.

***fac*-[(*m*-tarc)W(CO)$_3$]·0.5CH$_2$Cl$_2$ (7·0.5CH$_2$Cl$_2$).** A 160-mg (0.3-mmol) sample of 4 and 116 mg (0.3 mmol) of $(C_7H_8)W(CO)_3$ were added to 20 mL of dichloromethane and stirred at room temperature. The deep red solution turned yellow after 2 h. At this point only one product is detectable via TLC. Stirring was carried on for a total of 12 h. The solvent was removed in vacuo. The yellow residue was washed with hexane (removal of C_7H_8). The product was then purified by column chromatography (Al_2O_3/4% H_2O; CH_2Cl_2/petroleum ether, 1:1) to give 7 as a yellow powder. The compound can be crystallized from dichloromethane giving yellow crystals of 7·0.5CH$_2$Cl$_2$. The clear crystals turn opaque within 2 h (loss of CH_2Cl_2) (200 mg, 83% crystalline 7·0.5CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$): δ 7.29–6.59 (m, 12 H, Ar *H*), 3.38 (t, 6 H, C*H*$_2$O), 2.49 (t, 6 H, C*H*$_2$N), 1.62 (quint, 6 H, CH$_2$C*H*$_2$). ^{13}C{H} NMR (CDCl$_3$): δ 204.4 (CO), 161.6 (br, Ar–NC), 160.3, 130.9 (Ar *C*), 129.8 (br, Ar *C*–NC), 118.0, 116.7, 109.5 (Ar *C*), 64.4 (CH$_2$O), 48.9 (CH$_2$N), 27.1 (CH$_2$CH$_2$). Anal. Calcd for $C_{33.5}H_{31}ClN_4O_6W$ (7·0.5CH$_2$Cl$_2$, M_r = 804.94): C, 49.99; H, 3.88; N, 6.96. Found: C, 50.41; H, 3.92; N, 7.00.

General Procedure for the Preparation of Complexes *fac*-[(*o*-tarc)M(CO)$_3$] (8a–c). The preparation of the complexes is very similar and will be illustrated with the preparation of *fac*-[(*o*-tarc)W(CO)$_3$] (8c). Two solutions of 0.33 g (0.67 mmol) of 5 in 10 mL of CH_2Cl_2 and 0.24 g (0.67 mmol) of $(C_7H_8)W(CO)_3$ in 10 mL of CH_2Cl_2 were prepared. These solutions were added simultaneously to 10 mL of CH_2Cl_2 with stirring. Upon mixing, the deep red $(C_7H_8)W(CO)_3$ decolorized and a yellow solution formed. This solution was stirred for 2 h. The solvent was removed, and the residue was washed with hexane. The product was recrystallized from CH_2Cl_2, giving for all three metals the CH_2Cl_2-insoluble complex *fac*-[(*o*-tarc)M(CO)$_3$·HCl]. These complexes probably crystallize with 2.5 molecules of CH_2Cl_2 in the lattice, like the crystallographically characterized 8c·HCl·2.5CH$_2$Cl$_2$. The crystals loose CH_2Cl_2 very rapidly. Various amounts of CH_2Cl_2 can be detected, depending on the time of air exposure. To get reproducible microanalytical results, the compounds were isolated from the reaction mixture and dried at pump vacuum before conversion to the hydrochlorides *fac*-[(*o*-tarc)M(CO)$_3$·HCl] occurred (no recrystallization). This procedure was moderately successful. If the raw product is very impure, recrystallization step are necessary which lead to partial hydrochloride formation and poor microanalytical data.

8a: yellow powder, yield 0.32 g (76%). Anal. Calcd for $C_{33}H_{30}N_4O_6Cr$ (M_4 = 630.63): C, 62.85; H, 4.80; N, 8.88. Found: C, 63.87; H, 5.49; N, 7.56.

8b: yellow powder, yield 0.39 g (87%). Anal. Calcd for $C_{33}H_{30}N_4O_6Mo$ (M_r = 674.57): C, 58.76; H, 4.48; N, 8.31. Found: C, 57.86; H, 5.18; N, 7.19.

Table III. Summary of Crystal Structure Data[a]

	7·0.5CH$_2$Cl$_2$	8c·HCl·2.5CH$_2$Cl$_2$
formula	$C_{33.5}H_{31}ClN_4O_6W$	$C_{35.3}H_{36}Cl_6N_4O_6W$
fw	804.94	1011.27
cryst size, mm	0.35 × 0.25 × 0.17	0.40 × 0.32 × 0.11
cryst syst	monoclinic	triclinic
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
Z	8	2
a, Å	14.848 (3)	12.491 (4)
b, Å	26.016 (7)	13.414 (4)
c, Å	17.866 (5)	14.365 (2)
α, deg		114.73 (2)
β, deg	101.56 (2)	105.39 (2)
γ, deg		101.89 (2)
V, Å^3	6761 (3)	2102 (3)
d_c, g/cm^3	1.581	1.598
d_o, g/cm^3	1.57	1.58
radiation (λ, Å)	Mo Kα (0.71073)	
μ_c, cm^{-1}	33.7	32.4
2θ range, deg	$2 \leq 2\theta \leq 45$	
hkl range	$0 \leq h \leq 16$ $0 \leq k \leq 28$ $-17 \leq l \leq 18$	$0 \leq h \leq 13$ $-14 \leq k \leq 14$ $-16 \leq l \leq 16$
scan type	θ–2θ	
scan speed (θ), deg/min	min 1.5, max 29.30	min 1.7, max 6.7
no. of unique data	4038	5503
no. of obsd data	3208 [$I \geq 2\sigma(I)$]	5052 [$I \geq 3\sigma(I)$]
R, %	5.00	4.10
R_w, %	3.99	5.59
w	$2.13/\sigma(F_o)^2$	$[\sigma(F_o)^2]^{-1}$
no. of variables	413 (refined with SHELX76 in three blocks)	475 (refined with SDP in one block)
max shift/error	0.006	0.005
res electr dens	1.84 (near W)	1.7 (near W)
abs corr	empirical, DIFABS[b]	empirical, three ψ scans

[a] Estimated standard deviations are given in parentheses. [b] See ref 25.

8c: yellow powder, yield 0.35 g (69%). Anal. Calcd for $C_{33}H_{30}N_4O_6W$ (M_r = 762.48): C, 51.98; H, 3.97; N, 7.35. Found: C, 51.94; H, 4.22; N, 7.66.

[(talc)W(CO)$_3$] (9). The compound was prepared like the complexes 8a–c from 1.0 g (4.59 mmol) of 6 and 1.65 g (4.59 mmol) of $(C_7H_8)W(CO)_3$ in a total of 60 mL of CH_2Cl_2. In the course of the reaction 9 precipitates as yellow powder which is insoluble in CH_2Cl_2. Formation of a hydrochloride was not detected. Attempts to dissolve 9 in hot alcohols led to decomposition (1.11 g, 49%). Anal. Calcd for $C_{15}H_{18}N_4O_3W$ (M_r = 486.18): C, 37.06; H, 3.73, N, 11.52. Found: C, 37.06; H, 4.07; N, 10.69.

Crystal Structure Analyses. Crystals of 7·0.5CH$_2$Cl$_2$ and 8c·HCl·2.5CH$_2$Cl$_2$ were obtained at −26 °C from dichloromethane solutions. Both compounds are sensitive toward loss of dichloromethane from the crystals. Suitable specimens were selected with a device similar to that described by Veith and Bärnighausen[24] and transferred directly into the cold stream (−100 (5) °C) of an Enraf-Nonius CAD-4 (7·0.5CH$_2$Cl$_2$) or Syntex P2$_1$ (8c·HCl·2.5CH$_2$Cl$_2$) diffractometer. Important crystal and data collection details are listed in Table III. Data were collected at −100 (5) °C and reduced to structure factors (and their esd's) by correcting for scan speed, Lorentz, and polarization effects. No decay corrections were necessary. The data for 8c·HCl·2.5CH$_2$Cl$_2$ were corrected for absorption by means of three ψ scans, while an empirical absorption correction using the program DIFABS[25] was applied to the data for 7·0.5CH$_5$Cl$_2$. The structures were solved by standard Patterson methods, and all not disordered non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least squares using the programs of the SDP package[26] for 8c·HCl·2.5CH$_2$Cl$_2$ or SHELX76[27] for 7·0.5CH$_2$Cl$_2$. All hydrogens were added to the structure model on calculated

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Table IV. Fractional Coordinates for *fac*-[(*m*-tarc)W(CO)$_3$]•0.5CH$_2$Cl$_2$

atom	x	y	z	B_{eq},[a] Å^2
W	0.21582 (3)	0.18775 (1)	0.22091 (2)	2.85
Cl	0.0229 (2)	0.6113 (1)	0.3328 (2)	7.06
O1	0.4757 (4)	0.4255 (3)	0.3491 (4)	4.65
O2	0.1126 (4)	0.4634 (2)	0.2833 (3)	3.54
O3	0.2592 (6)	0.3791 (3)	0.5332 (4)	4.46
O4	0.2826 (6)	0.0797 (3)	0.2951 (4)	5.31
O5	0.2800 (6)	0.1637 (3)	0.0656 (5)	6.55
O6	0.0182 (6)	0.1435 (3)	0.1557 (6)	7.74
N1	0.3081 (5)	0.4869 (3)	0.4341 (5)	3.20
N2	0.4036 (6)	0.2465 (3)	0.3007 (5)	3.64
N3	0.1594 (6)	0.3040 (3)	0.1615 (5)	3.87
N4	0.1515 (5)	0.2366 (3)	0.3683 (5)	3.29
C1	0.3406 (9)	0.2248 (4)	0.2699 (6)	4.10
C2	0.4658 (6)	0.2858 (4)	0.3334 (5)	2.73
C3	0.5530 (7)	0.2725 (4)	0.3703 (5)	3.35
C4	0.6104 (6)	0.3317 (5)	0.4007 (5)	4.18
C5	0.5843 (7)	0.3621 (4)	0.3928 (6)	3.90
C6	0.4959 (7)	0.3744 (4)	0.3541 (6)	3.86
C7	0.4356 (7)	0.3361 (4)	0.3230 (5)	3.18
C8	0.3872 (7)	0.4411 (4)	0.3074 (6)	4.49
C9	0.3773 (8)	0.4975 (4)	0.3182 (7)	4.50
C10	0.3809 (7)	0.5107 (4)	0.4027 (7)	4.59
C11	0.1768 (6)	0.2612 (4)	0.1789 (5)	3.39
C12	0.1441 (7)	0.3569 (4)	0.1572 (6)	3.37
C13	0.1382 (7)	0.3827 (4)	0.0889 (6)	4.18
C14	0.1259 (7)	0.4349 (4)	0.0888 (6)	4.37
C15	0.1186 (6)	0.4615 (4)	0.1538 (5)	3.31
C16	0.1233 (5)	0.4340 (3)	0.2220 (5)	2.32
C17	0.1349 (6)	0.3810 (3)	0.2248 (5)	2.96
C18	0.1279 (6)	0.4393 (3)	0.3567 (5)	2.73
C19	0.1374 (6)	0.4822 (4)	0.4164 (5)	3.42
C20	0.2215 (6)	0.5155 (3)	0.4131 (5)	3.43
C21	0.1740 (6)	0.2156 (3)	0.3172 (6)	2.73
C22	0.1393 (7)	0.2712 (4)	0.4249 (5)	3.12
C23	0.0595 (7)	0.2708 (4)	0.4526 (6)	3.45
C24	0.0508 (8)	0.3066 (4)	0.5080 (6)	4.69
C25	0.1169 (8)	0.3420 (4)	0.5335 (6)	4.43
C26	0.1974 (8)	0.3424 (4)	0.5051 (5)	3.26
C27	0.2099 (7)	0.3069 (3)	0.4501 (5)	2.84
C28	0.3423 (7)	0.3821 (4)	0.5045 (6)	4.22
C29	0.3920 (7)	0.4312 (4)	0.5365 (7)	4.89
C30	0.3345 (7)	0.4790 (4)	0.5166 (6)	4.12
C31	0.2596 (7)	0.1199 (4)	0.2679 (6)	3.86
C32	0.2580 (7)	0.1722 (3)	0.1240 (7)	3.80
C33	0.0908 (9)	0.1596 (4)	0.1807 (7)	4.51
C34[b]	0.000 (0)	0.5749 (6)	0.2500 (0)	6.93

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$. [b] C34 is the carbon atom of the dichloromethane molecule; it resides on the 2-fold axis, Wyckoff position e, SOF 0.5.

Table V. Fractional Coordinates for *fac*-[(*o*-tarc)W(CO)$_3$•HCl]•2.5CH$_2$Cl$_2$

atom	x	y	z	B_{eq},[a] Å^2
W	0.19513 (2)	0.00388 (2)	0.19191 (2)	1.901
Cl1	0.6180 (1)	−0.4786 (1)	0.1744 (1)	2.97
Cl2	0.1067 (2)	0.1819 (2)	0.6886 (2)	4.93
Cl3	0.1393 (2)	0.2038 (2)	0.5156 (2)	6.21
Cl4	0.3612 (3)	0.5989 (2)	0.5690 (2)	9.2
Cl5	0.5558 (2)	0.5544 (3)	0.6772 (2)	10.11
Cl6	0.071 (1)	0.528 (1)	0.610 (1)	19.2*[b]
Cl7	0.006 (2)	0.661 (1)	0.606 (1)	22.7*
O1	0.4331 (4)	−0.1365 (3)	0.4438 (3)	3.1
O2	0.1084 (3)	−0.4588 (4)	−0.0291 (3)	3.0
O3	0.5730 (3)	−0.0726 (3)	0.1026 (3)	2.6
O4	0.2875 (5)	0.2649 (5)	0.3761 (4)	5.7
O5	−0.0508 (4)	−0.0125 (5)	0.2128 (4)	5.5
O6	0.1301 (4)	0.1044 (4)	0.0406 (3)	4.6
N1	0.4650 (4)	−0.3337 (4)	0.1685 (4)	2.3
N2	0.2611 (5)	−0.0679 (4)	0.3730 (4)	3.1
N3	0.0634 (4)	−0.2655 (5)	−0.0060 (4)	2.9
N4	0.4437 (4)	0.0579 (4)	0.1563 (3)	2.5
C1	0.2411 (5)	−0.0471 (5)	0.3051 (5)	2.8
C2	0.2692 (6)	−0.0846 (5)	0.4578 (4)	2.7
C3	0.1884 (6)	−0.0651 (6)	0.0547 (5)	3.2
C4	0.1950 (6)	−0.0860 (7)	0.5858 (5)	3.9
C5	0.2812 (7)	−0.1258 (7)	0.6199 (5)	4.3
C6	0.3657 (6)	−0.1407 (6)	0.5769 (5)	3.4
C7	0.3590 (5)	−0.1205 (5)	0.4948 (4)	2.5
C8	0.5006 (6)	−0.2088 (5)	0.4533 (5)	3.0
C9	0.5439 (5)	−0.2362 (5)	0.3666 (5)	2.9
C10	0.4364 (5)	−0.3007 (5)	0.2631 (4)	2.4
C11	0.1157 (5)	−0.1708 (5)	0.0665 (4)	2.5
C12	−0.0031 (5)	−0.3710 (6)	−0.1000 (5)	3.1
C13	−0.0903 (6)	−0.3731 (6)	−0.1798 (5)	3.7
C14	−0.1534 (7)	−0.4792 (7)	−0.2740 (6)	4.5
C15	−0.1320 (6)	−0.5787 (7)	−0.2869 (5)	4.2
C16	−0.0438 (6)	−0.5782 (6)	−0.2065 (5)	3.6
C17	0.0221 (5)	−0.4709 (6)	−0.1115 (4)	2.8
C18	0.1568 (5)	−0.5492 (5)	−0.0435 (5)	2.9
C19	0.2634 (5)	−0.5004 (5)	0.0567 (5)	2.7
C20	0.3533 (5)	−0.3924 (5)	0.0721 (4)	2.6
C21	0.3576 (5)	0.0314 (5)	0.1702 (5)	2.5
C22	0.5449 (5)	0.1056 (5)	0.1442 (4)	2.2
C23	0.5750 (6)	0.2166 (5)	0.1573 (5)	3.2
C24	0.6788 (6)	0.2641 (6)	0.1495 (5)	4.0
C25	0.7491 (6)	0.1975 (6)	0.1266 (5)	3.8
C26	0.7184 (5)	0.0867 (5)	0.1103 (4)	2.8
C27	0.6146 (5)	0.0369 (5)	0.1182 (4)	2.1
C28	0.6505 (5)	−0.1380 (5)	0.0969 (5)	2.8
C29	0.5812 (5)	−0.2538 (5)	0.0848 (5)	3.0
C30	0.5465 (5)	−0.2268 (5)	0.1770 (4)	2.5
C31	0.2571 (5)	0.1689 (5)	0.3086 (5)	2.9
C32	0.0409 (6)	−0.0099 (6)	0.2051 (5)	3.7
C33	0.1519 (5)	0.0652 (5)	0.0948 (5)	3.0
C34	0.1119 (7)	0.2693 (7)	0.6294 (6)	4.8
C35	0.402 (1)	0.5040 (7)	0.6089 (6)	6.9
C36	0.010 (2)	0.577 (2)	0.503 (2)	8.1*
HN1	0.508 (7)	−0.364 (7)	0.170 (6)	4.0

[a] See footnote *a* in Table IV. [b] Starred atoms (C36, Cl6, Cl7) are the atoms of the disordered dichloromethane molecule and were refined isotropically. The isotropic temperature factor for HN1 was held constant during refinement at B_{eq} = 4.0 Å^2.

positions [d(C–H) = 0.95 Å],[28] with the exception of HN1 in **8c**·HCl·2.5CH$_2$Cl$_2$, which was found in a difference Fourier map. The positional parameters of this atom were refined in the least-squares procedure with a fixed isotropic temperature factor $B_{iso,H}$ = 4.0 Å^2. The isotropic temperature factors for all other hydrogens on calculated positions were fixed to be 1.3 times the B_{eq} of the parent carbon atom (for **8c**·HCl·2.5CH$_2$Cl$_2$) or to be $U_{iso,H}$ = 0.08 Å^2 (for **7**·0.5CH$_2$Cl$_2$). The dichloromethane molecule in **7**·0.5CH$_2$Cl$_2$ resides on a special position of the 2-fold axis and is shared between two asymmetric units. Crystals of **8c**·HCl·2.5CH$_2$Cl$_2$ contain two molecules of dichloromethane on general positions. A third dichloromethane molecule was found on a position close to (but not on) an inversion center. This molecule (C36, Cl6, Cl7) is disordered between two asymmetric units, and its positional parameters were refined with site occupancy factors of 0.5. No hydrogen positions were calculated for the disordered dichloromethane molecule. ORTEP[29] was used for all molecular drawings. Atomic coordinates and equivalent isotropic thermal parameters are listed in Tables IV and V.

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Registry No. **1**, 137145-24-5; **2**, 137145-25-6; **3**, 137145-26-7; **4**, 137145-27-8; **5**, 137145-28-9; **6**, 2456-97-5; **7**·$^1/_2$CH$_2$Cl$_2$, 137167-86-3; **8a**·HCl, 137167-84-1; **8b**·HCl, 137195-81-4; **8c**·HCl·2.5CH$_2$Cl$_2$, 131457-45-9; **9**, 131457-41-5; (C$_7$H$_8$)W(CO)$_3$, 12128-81-3; (C$_7$H$_8$)Cr(CO)$_3$, 12125-72-3; (C$_7$H$_8$)Mo(CO)$_3$, 12125-

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77-8; 3-nitrophenol, 554-84-7; tris(3-chloropropyl)amine, 79189-90-5; acetic formic anhydride, 2258-42-6; diphosgene, 503-38-8.

Supplementary Material Available: Tables listing all bond distances and angles, anisotropic thermal parameters, and hydrogen positions and ORTEP plots of both molecular structures with the employed numbering scheme for $7\cdot0.5CH_2Cl_2$ and $8c\cdot HCl\cdot2.5CH_2Cl_2$ (13 pages); tables of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

Mechanism of Homogeneous Hydrosilation of Alkenes by (η^5-Cyclopentadienyl)rhodium

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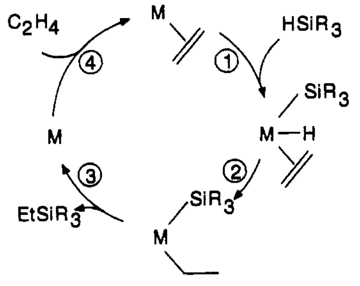
The mechanism of hydrosilation of ethene with R_3SiH catalyzed by $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(SiR_3)H$ (principally with R = Et) has been studied by NMR and GC/MS methods. Comparison with related compounds indicates that activity is confined to this group of compounds at room temperature. The mercury test demonstrates that the reaction is homogeneous, in contrast to recent evidence on platinum catalysts. The reaction mechanism was investigated by deuterium labeling of either substrate and variation of alkene and trialkylsilane. These experiments demonstrated conclusively that $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(SiR_3)H$ acts as a precursor to the catalytically active species but is not within the catalytic cycle. In consequence, the Chalk–Harrod mechanism cannot apply in this system. An alternative cycle is proposed which is initiated by a hydrogen shift to form $(\eta^5\text{-}C_5H_5)Rh(C_2H_5)(SiR_3)$. The latter generates the hydrosilation products via oxidative addition of R_3SiH to form an intermediate containing two silicon atoms. The initial hydrogen shift is consistent with studies of intramolecular exchange and stoichiometric reactions of the starting material. The mechanism is equivalent to the one proposed by Wrighton and Seitz for hydrosilation catalyzed by cobalt carbonyls.

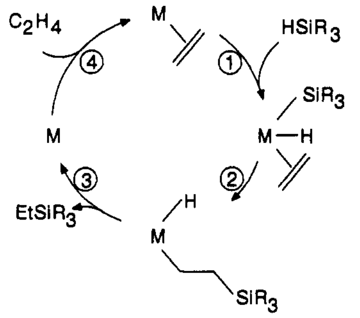
Introduction

Many recent reviews and papers, in common with their predecessors, explain the catalytic mechanism of hydrosilation by the Chalk–Harrod cycle or one of its variants.[1] In the first step of these mechanisms, a metal alkene complex is converted to a metal alkene silyl hydride complex.[2] It follows that a complex conforming to the latter description is unlikely to be isolable. In a communication published in 1985, we reported the characterization of $CpRh(C_2H_4)(SiR_3)H$ (1) formed on photolysis of $CpRh(C_2H_4)_2$ in the presence of R_3SiH (R = Me, Et; Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5).[3] This molecule contains all the essential ligands for the key intermediate in the Chalk–Harrod mechanism of hydrosilation. Moreover, we showed that its formation is accompanied by hydrosilation and silation products. In subsequent work, we showed that 1 could be obtained in high yield without hydrosilation products by carrying out the photolysis at low temperature.[4] We also examined the stoichiometric reactivity of 1 toward ethene, trialkylsilanes, and other ligands under photochemical and thermal conditions.[5] We now report the catalytic reactivity of 1 toward alkenes and trialkylsilanes together. Isotopic labeling is used to probe the reaction mechanism and to show that hydrosilation in this case does not proceed via the Chalk–Harrod mechanism or variants involving silyl migration (Schemes I and II).

Scheme I. Chalk–Harrod Mechanism of Hydrosilation



Scheme II. Variant on Chalk–Harrod Mechanism for Hydrosilation with Silyl Migration



The Chalk–Harrod mechanism employs conventional oxidative-addition/reductive-elimination steps to explain hydrosilation (Scheme I).[1] Oxidative addition of R_3SiH to a metal alkene complex, usually with a d^8 configuration (step 1), is followed by migration of the hydride onto the

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