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(Diazomethyl)silyl-functionalized Fischer-type carbene complexes

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Abstract

The synthesis of two types of so far unknown title compounds is described. Carbene complexes $L_nM{=}C(R)O{-}SiR_2{-}C(N_2)COOMe$ [$L_nM{=}(OC)_5W$ (**3**), $(OC)_5Cr$ (**4**), $(OC)_5Mo$ (**5**), $(MeCp)(OC)_2Mn$ (**6**)] were obtained from the corresponding acyl metalates by electrophilic (diazomethyl)silylation. Similarly, (diazomethyl)silylation of lithiated dicarbonyl(η^5-methylcyclopentadienyl)(1-ethoxyethylidene)manganese yielded a manganese carbene complex (**8a**) with $CH_2{-}SiR_2{-}C(N_2)COOMe$ substitution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fischer-type carbene complexes; Diazo compounds; Silyl triflates

1. Introduction

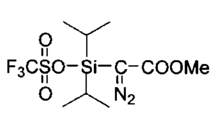
Aliphatic diazo compounds are undoubtedly the most important and versatile carbene transfer reagents [1]. While their photochemical and thermal dediazoniation provide access to free carbenes, N_2 extrusion by transition-metal catalysts [2] (especially based on Cu, Rh, Pd, and Ru) generates short-lived metal–carbene complexes which may also be considered as metal-stabilized carbenium ions and which represent the proper carbene-transfer reagents. The analogy, both in electronic structure and reactivity, between these intermediate metal–carbene complexes and the stable carbene complexes of the Fischer type [3] is undeniable. Perhaps the most obvious manifestation of Fischer-type carbene complexes to act as carbene transfer reagents is their ability to cyclopropanate olefinic substrates [4].

Previous to our work [5], the synthesis of diazo-functionalized Fischer-type carbene complexes, featuring the combination of two familiar carbene transfer functions in one molecule, has not been reported. We present here the synthesis of Fischer-type carbene complexes in which a diazomethyl function is separated from the carbenic carbon atom by either an $OSiR_2$ or a CH_2SiR_2 unit.

2. Results and discussion

2.1. (Diazomethyl)silyloxy-substituted carbene complexes

Complexes of this type were prepared according to the classical recipe to prepare alkoxycarbene [3,6] and siloxycarbene [7] complexes of chromium, molybdenum, and tungsten, namely nucleophilic alkylation of $M(CO)_6$ followed by electrophilic *O*-alkylation (*O*-silylation) of the acyl metalate intermediate. For our purpose, we used silyl triflate (**1**) [8] as an electrophilic (diazomethyl)silylation reagent.



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Silyl triflate (**1**) was added at −40°C to a suspension of the yellow acetyl tungstate (**2a**), obtained from hexacarbonyltungsten and methyl lithium (Scheme 1). When this mixture was allowed to assume 0°C, a deep-red color indicative of the tungsten carbene complex (**3a**) developed which was isolated as a solid in 12% yield by evaporation of the volatiles and extraction into pentane at −20°C. The IR spectrum of **3a** confirmed the presence of a diazo function ($\nu(N_2) = 2080\ cm^{-1}$) and a $W(CO)_5$ moiety ($\nu(CO) = 2060$, 1974, 1941 cm^{-1}). The ^{13}C-NMR chemical shifts of W=C ($\delta =$

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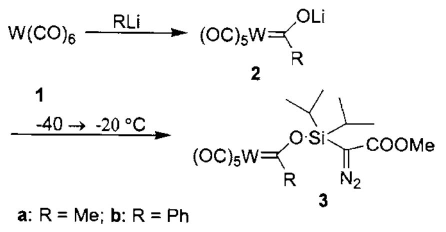
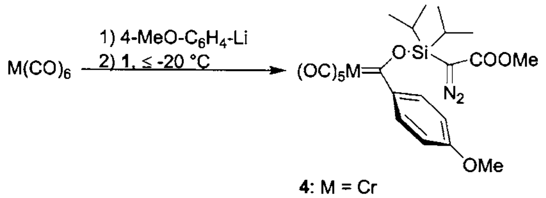


Scheme 1.



Scheme 2.

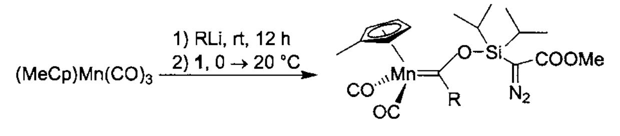
345.6 ppm), *cis*-CO (198.1 ppm) and *trans*-CO (206.1 ppm) are in close agreement with the values reported for the related carbene complex $(OC)_5W{=}C(Me)OSiMe_3$ [7]. In the ^{13}C-NMR spectrum, recorded at −10°C in toluene-d_8, a second, less intense set of signals was present ($\delta = 344.2$, 204.8, 198.8 ppm for the carbon atoms mentioned before). As for other carbene complexes [9], this points to the presence of *s-trans*- and *s-cis*-isomers with respect to the $C_{carbene}$–O bond, and similar to complexes of the type $(OC)_5Cr{=}C(Ph)OSi(^iPr_2)OR$ [10] it may be assumed that the *s-trans*-isomer prevails. Line broadening of the signals of the diazo and ester carbon atoms indicates that another dynamic process, namely rotation around the $C(N_2)$–$C({=}O)$ bond, is also slowed down at this temperature.

According to the ^{13}C-NMR spectrum, complex **3a** contained small amounts of impurities. However, purification was not possible since **3a** did not survive column chromatography at −30°C on silica gel or alumina and since it rapidly underwent unspecific decomposition above 0°C. The related benzylidenetungsten complex (**3b**), prepared similarly to **3a**, is also thermolabile above 0°C. In contrast to **3a**, it could be recovered partially after passing a silica gel column at −30°C, but this method did not allow a complete separation from impurities. In the ^{13}C-NMR spectrum, the signals at $\delta = 322.9$ (W=C), 197.1 (*cis*-CO), and 203.4 ppm (*trans*-CO) confirm the presence of the metal carbene functionality.

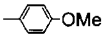
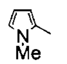
Tungsten carbene complexes typically have a higher thermal stability than the related complexes of chromium and molybdenum [4,9]; however, an electron-donating aromatic substituent at the carbenic carbon atom enhances the thermodynamic stability of the latter considerably [9]. Therefore, we chose to prepare 4-anisyl-substituted chromium (**4**) and molybdenum (**5**) carbene complexes as shown in Scheme 2. In both cases, however, this procedure was disappointingly ineffective. Complex **4** could be extracted in low yield from the reaction mixture with pentane at −10°C, but not in pure form. The presence of **4** was established by the ^{13}C-NMR signal at $\delta = 348.4$ ppm (Cr=C) and the molecular ion peak in the EI mass spectrum ($m/z = 540$). Complex **5** was obtained in low yield (5%) as a dark-red oil after column chromatography on silica gel at −30°C; a sample that was stored at −78°C underwent decomposition already after a few days as indicated by a color change from red to black. The ^{13}C-NMR spectrum at −20°C showed, besides some impurities (signals in the aliphatic and aromatic region), the presence of two metal carbene species, most likely again the *s-trans*- and *s-cis*-isomers with respect to the $C_{carbene}$–O bond, characterized by chemical shifts at $\delta = 323.0/327.0$ (Mo=C), 213.8/215.7 (*trans*-CO) and 207.0/206.8 ppm (*cis*-CO).

The difficulty in isolating carbene complexes **3**–**5** and their thermolability is not totally unexpected. Since complexes of the type $(OC)_5W{=}C(Ar)OSiMe_3$ are known to undergo readily a nucleophile-assisted cleavage of the O–Si bond [7,11], it cannot be excluded that **3**–**5** behave similarly, in spite of the presence of the bulkier ^{i}Pr substituents at silicon, under the conditions of chromatographic workup and in the presence of traces of water in general. The thermolability may have several causes, one of them being the intrinsic incompatibility of the metal carbene and the diazo functionalities. The M=C bond in carbene complexes of Cr, Mo, and W is strongly polarized, and the electrophilic carbon may induce diazo decomposition by interaction with the nucleophilic diazo carbon atom. In fact, it is known that the stable tungsten carbene complex $(OC)_5W{=}C(OMe)Ph$ is able to eliminate N_2 from diazoalkanes and ethyl diazoacetate [12]. Therefore, our attention was drawn to dicarbonyl(cyclopentadienyl)manganese carbene complexes. Since the $Cp(CO)_2Mn$ fragment is a stronger π donor than the pentacarbonyl metal moiety, the bond order of the Mn=C bond is higher and the carbon atom is less electrophilic [13]. Consequently, manganese complexes are far less reactive across the metal–carbene bond than the $M(CO)_5$ carbene complexes of Cr, Mo, and W [14]. In the literature, a few siloxy-substituted manganese carbene complexes have been described as viscous red oils of limited stability [14b,15].

Reaction of tricarbonyl(methylcyclopentadienyl)manganese with an organolithium compound followed by silylation with **1** afforded manganese carbene complexes (**6a**–**f**) as viscous deep-red oils (Scheme 3, Table 1) which could by handled indeed more easily than complexes **3**–**5**. Purification by column chromatography on silica gel at -30°C should be possible in principle, but we found it necessary to make a compromise between keeping the loss of product (by decomposition on the column) low and achieving a complete separation of **6** from residual (MeCp)Mn(CO)$_3$. Therefore, in almost all cases no satisfactory elemental analyses could be obtained. Complexes **6** are rather thermally stable at 25°C, but must be handled with rigorous exclusion of moisture and air. On prolonged storing, paramagnetic impurities are formed which cause considerable line broadening in the NMR spectra of such samples but can be removed by filtering their solutions over a pad of kieselguhr.



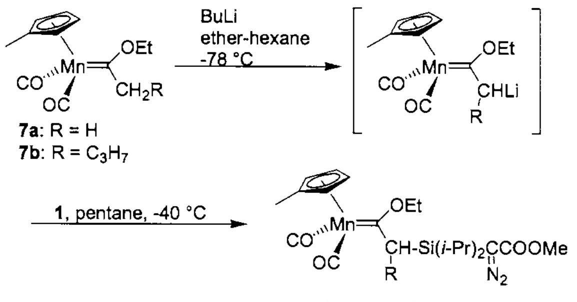
6

6	a	b	c	d	e	f
R	Me	Bu	Ph			
Yield, %	61	47	80	69	23	72

Scheme 3.

Table 1
Diagnostic ^{13}C-NMR signals of manganese carbene complexes **6** (CDCl$_3$, δ/ppm)

6	R	Mn=C	Mn–CO	CN$_2$	COOMe
a	Me	339.6	232.8	44.0	168.5
b	Bu	346.6	232.8	44.6	168.5
c	Ph	334.0	231.9	44.2	168.5
d	4-Methoxyphenyl	327.9	232.2	44.8	167.9
e	2-Furyl	348.3	232.5 234.4	45.0	164.0
f	1-Methylpyrrol-2-yl	324.3	232.0 232.2	44.5	169.4



7a: R = H
7b: R = C$_3$H$_7$

8a: R = H (43%)
8b: R = C$_3$H$_7$ (0%)

Scheme 4.

The constitution of **6a**–**f** is fully supported by their IR, NMR, and mass spectra. The IR spectra show intense absorptions caused by the stretching vibrations of the diazo group ($\nu = 2080$–2100 cm^{-1}) and the carbonyl ligands (1940–1970 and 1880–1900 cm^{-1}). The ^{13}C-NMR spectra could be recorded in CDCl$_3$ at 25°C, and their diagnostic signals are given in Table 1. Other than in the case of **3a** and **5**, a second isomer (due to slow rotation around the C$_{\text{carbene}}$–O bond) was not observed when the ^{13}C-NMR spectra were recorded at -25 ± 5°C; only dynamic line broadening of the CN$_2$ and COOMe signals was noted in some cases. The occurrence of separate signals for each of the two carbonyl ligands in the case of **6e** and **f** is unusual; it indicates that the mirror plane of the (MeCp)Mn(CO)$_2$ fragment does not extend to the carbene ligand. It is known that complexes of the types CpMn(CO)$_2$=C(OR^1)R^2 (R^2=Ph [13a,14b], vinyl [16]) and (η^5-cyclohexadienyl)Mn(CO)$_2$=C(OEt)aryl [17]) in the solid state exhibit a variety of different conformations around the three bonds involving the C$_{\text{carbene}}$ atom. In the case of aryl and hetaryl-substituted complexes **6c**–**f**, steric interactions between the bulky Si^{i}Pr$_2$ group and neighboring groups are minimized when an *s-trans* conformation at the C$_{\text{carbene}}$–O bond is given and when at the same time the (het)aryl ring is approximately perpendicular to the O–C$_{\text{carbene}}$–C$_{\text{(het)aryl}}$ plane. In this conformation, the two isopropyl substituents at Si may still prevent the 2-furyl and 2-pyrrolyl ring from rotating, thus rendering the two carbonyl groups diastereotopic even when the conformation around the Mn–C$_{\text{carbene}}$ bond is the most common one in such manganese carbene complexes [13a], namely with the C$_{\text{hetaryl}}$–C$_{\text{carbene}}$–O plane bisecting the OC–Mn–CO angle. It should be added that temperature-dependent ^{13}C-NMR spectra between -25 and $+30$°C did not reveal a dynamic exchange for the two CO signals.

Mass spectra (CI mode) of **6c** and **e** showed the molecular ion as the base peak. Similar to other siloxycarbene complexes with the (MeCp)(CO)$_2$Mn moiety [15], it appears that the two carbonyl ligands are lost in one step, and a fragment formed by loss of 2CO and N$_2$ was also observed.

2.2. (Diazomethyl)silylmethyl-substituted carbene complexes

The approach to these complexes takes advantage of the C–H acidity of alkyl-substituted Fischer carbene complexes [16,18]. Deprotonation of **7a** with butyl lithium followed by C-silylation with (trifloxysilyl)diazoacetate (**1**) provided the organometallic diazoacetate (**8a**) (Scheme 4) which was obtained as a deep-red oil after chromatographic purification on silica gel at -30°C. The compound is stable in substance and in dry non-protic solvents at least for several weeks. The composition of **8a** follows from the analytical and spectroscopic data. The IR spectrum showed the expected absorptions for the stretching vibrations of the diazo group (2080 cm^{-1}) and the two carbonyl ligands (1940, 1875 cm^{-1}). In the ^{13}C-NMR spectrum, the resonance of the carbenic carbon atom ($\delta = 337.9$ ppm) appeared at slightly lower field (ca. 2 ppm) than in **7a**. The value of the $^1J(^{13}C,^1H)$ coupling constant of the α-CH$_2$ carbon ($\delta = 48.6$ ppm, $J = 122$ Hz) was lower by 6 Hz than in **7a**, in agreement with the expected [19] inductive effect of the silyl group.

Efforts to prepare diazoacetate (**8b**) from **7b** by deprotonation with BuLi and subsequent addition of **1** were unsuccessful, probably because the S$_N$ reaction at silicon failed due to steric hindrance. Analogous workup as for **8a** gave only unchanged **7b** besides small amounts of an unidentified product.

3. Conclusions

We have presented here the synthesis of two types of novel diazo-functionalized Fischer-type carbene complexes, in which a diazomethyl function is separated from the metal–carbene either by a OCH_2SiR_2 or by a CH_2SiR_2 moiety. It is worth noting that the metal–carbene function (with an electrophilic carbon atom) and the diazo functionality (with a nucleophilic carbon atom) tolerate each other in the same molecule, but the low thermal stability of the M(CO)$_5$ complexes **3**–**5** suggests that the compatibility is limited. The synthetic potential of these diazo-functionalized carbene complexes is still to be evaluated.

4. Experimental

All reactions were carried out under argon in glassware that had been evacuated, heated with a heat gun, and filled with argon prior to use. Solvents were dried by standard procedures and stored under argon. Column chromatography was performed on silica gel (Macherey&Nagel, 0.063–0.2 mm) which had been dried during 2 days at 220°C/0.002 mbar and then deactivated by treatment with 3% (w/w) of water. For low-temperature column chromatography, a cooling liquid was circulated through the outer chamber of a two-walled glass column. NMR spectra were recorded on Bruker AC 200 (^{1}H: 200.1 MHz) and AMX 400 instruments (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz). The solvents used were stored over molecular sieves (4 Å) and saturated with argon before use. Internal standards were used (^{1}H: TMS; ^{13}C: CDCl$_3$, $\delta = 77.0$; toluene-d_8, $\delta = 20.4$). IR spectra were recorded on Perkin–Elmer 1310 and 397 spectrophotometers. Mass spectra were obtained with a Varian MAT 311A instrument.

*4.1. Preparation of silyl triflate (**1**)*

The literature procedure [8] was modified as follows: a stirred solution of diisopropylsilyl bis(trifluoromethanesulfonate) (2.04 g, 1.46 ml, 5.0 mmol) in pentane (20 ml) was cooled at 0°C, and a solution of diisopropylethylamine (0.74 g, 1.0 ml, 5.7 mmol) and methyl diazoacetate (0.50 g, 5.0 mmol) in ether (5 ml) was gradually added. The mixture was brought to room temperature (r.t.) and stirring continued for 3 h. The precipitated ammonium triflate was separated by filtration (sintered glass filter funnel) and rinsed with pentane (2 × 10 ml). The solution was concentrated to a volume of 10 ml and used directly for the silylation reactions.

*4.2. Pentacarbonyl{[1-[diazo(methoxycarbonyl)methyl]-diisopropylsilyloxy]ethylidene}tungsten (**3a**)*

MeLi in ether (1.6 M, 2.50 ml, 4.0 mmol) was added to a suspension of W(CO)$_6$ (1.45 g, 4.1 mmol) in pentane (100 ml) at r.t. A yellow precipitate formed. The mixture was refluxed for 90 min, then cooled at −40°C. A freshly prepared solution of silyl triflate (**1**) (4.0 mmol) in pentane–ether (4.0 mmol) was gradually added. The mixture was then allowed to warm up to 0°C within 6 h, thereby developing a deep-red color. The solvent was evaporated at −20°C/0.002 mbar, and the semi-solid residue was extracted with pentane (2 × 40 ml). The extracts furnished **3a** as a red solid (280 mg, 12%) which is both moisture-sensitive and thermolabile. Unspecific decomposition started above 0°C after a few min and was indicated by a color change from red to black. IR (pentane solution): $\nu = 2080$ (s), 2060 (s), 1974 (vs), 1941 (vs), 1685 (m) cm^{-1}. ^{13}C-NMR (toluene-d_8, −10°C): signals for two isomers (major/minor), see text; $\delta = 13.4$ and 13.9 (SiCH), 16.5–16.8 (4 signals, CH*Me*$_2$), 44.0 (broad, C=N$_2$), 52.8 (OMe), 55.0/55.6 (W=C*Me*), 169.0 (broad, ester C=O), 191.1/191.8 (*cis*-CO), 206.1/204.8 (*trans*-CO), 345.6/344.2 (W=C).

*4.3. Pentacarbonyl{1-[[diazo(methoxycarbonyl)methyl]-diisopropylsilyloxy]benzylidene}tungsten (**3b**)*

A solution of phenyl lithium in cyclohexane–ether (2 M, 2.50 ml, 5.0 mmol) was added to a suspension of W(CO)$_6$ (1.80 g, 5.1 mmol) in ether (50 ml). The mixture was stirred for 3 h, cooled at −30°C, and a solution of **1** (5.0 mmol) in pentane–ether (10 ml) was added gradually. After a further 6 h between −30 and −10°C, the volatiles were evaporated at −10°C/0.003 mbar. The remaining red–brown solid was extracted with pentane (3 × 30 ml) and cooled at −30°C. The combined extracts were concentrated and subjected to column chromatography on silica gel (60 g) at −30°C. Elution with pentane–ether (2:1) furnished a dark-red oil (180 mg) which contained **3b** and some impurities. Further purification was not possible due to the thermolability of the complex as described for **3a**. IR (pentane solution): $\nu = 2080$ (s), 1975 (vs), 1950 (m), 1940 (s), 1920 (s), 1670 (m) cm^{-1}. ^{13}C-NMR (toluene-d_8, -20°C): $\delta = 13.8$ (SiCH), 16.8 and 17.1 (CHMe_2), 41.9 (C=N$_2$), 51.5 (OMe), 126.3 (*m*-C), 128.3 (*o*-C), 130.7 (*p*-C), 156.2 (*i*-C), 169.8 (C=O), 197.1 (*cis*-CO), 203.4 (*trans*-CO), 322.9 (W=C).

*4.4. Pentacarbonyl{1-[[diazo(methoxycarbonyl)methyl]-diisopropylsilyloxy](4-methoxyphenyl)methylene}-chromium **(4)***

A solution of 4-methoxyphenyl lithium in ether (10 ml), prepared from 1-bromo-4-methoxybenzene (1.05 g, 5.6 mmol) and BuLi (1.6 M in ether, 5.5 mmol) at -25°C, was added to a stirred suspension of Cr(CO)$_6$ (1.32 g, 6.0 mmol) in ether (25 ml). The red mixture was stirred for another 90 min at 0°C, then cooled at -20°C, and silyl triflate **1** (5.0 mmol) in pentane (10 ml) was gradually added. The color changed immediately from red to dark-red. When the addition was complete, stirring was continued for 30 min, the solvent was evaporated at -10°C/0.003 mbar, and the residue was extracted with pentane (4×10 ml) cooled at -10°C. The combined extracts were concentrated to leave a dark-red residue (130 mg) which consisted of **4** and some unidentified impurities. ^{13}C-NMR (toluene-d_8, -10°C): $\delta = 13.6$ (SiCH), 16.7 and 16.9 (CHMe_2), 43.0 (br, C=N$_2$), 50.9 (COOMe), 51.7 (Ar–OMe), 112.8 (*m*-C), 129.4 (*o*-C), 160.2 (C$_{\text{aryl}}$–OMe), 169.5 (br, C=O), 214.2 (*cis*-CO), 348.4 (Cr=C); identification of *i*-C$_{\text{aryl}}$ and *trans*-CO not possible due to impurities. MS (EI, 70 eV): $m/z = 540$ (1%) [M$^+$], 375 (13), 361 (17), 287 (9), 264 (19), 263 (100).

*4.5. Pentacarbonyl{1-[[diazo(methoxycarbonyl)methyl]-diisopropylsilyloxy](4-methoxyphenyl)methylene}-molybdenum **(5)***

Preparation from 4-methoxyphenyl lithium, Mo(CO)$_6$, and **1** as described for **4**, and column chromatography as described for **3b** (all manipulations at -25 to -30°C) afforded a dark-red oil (150 mg) of **5** and some impurities. Further purification was not possible due to the thermolability of the complex; even on storing at -78°C, a color change from red to black occurred after a few days. IR (pentane solution): $\nu =$ 2090 (s), 2010 (sh), 1975 (s, br), 1880 (sh), 1685 (s) cm^{-1}. ^{13}C-NMR (toluene-d_8, -20°C): Signals for two isomers (major/minor), see text; $\delta = 13.5$ and 14.6 (SiCH); 15.5, 16.8, 17.0, 17.6 (CHMe_2); 41.0 (br, C=N$_2$), 52.3 (COOMe), 54.4 (Ar–OMe), 114.1 (*m*-C), 132.5 (*o*-C), 142.1 (*i*-C), 165.8 (C$_{\text{aryl}}$–OMe), 171.0 (br, C=O), 207.0/206.8 (*cis*-CO), 213.8/215.7 (*trans*-CO), 323.0/327.0 (Mo=C).

*4.6. {1-[[Diazo(methoxycarbonyl)methyl]diisopropylsilyloxy]ethylidene}dicarbonyl(methylcyclopentadienyl)-manganese **(6a)***

A solution of MeLi in ether (1.6 M, 6.25 ml, 10.0 mmol) was added at r.t. to a solution of (C$_5$H$_4$Me)(CO)$_3$Mn (2.18 g, 1.58 ml, 10.0 mmol) in ether (20 ml). An orange-colored precipitate formed while the solution assumed an olive-green color. After 12 h, the mixture was cooled at 0°C and a solution of **1** (10.0 mmol) in pentane (10 ml) was added, causing an immediate color change to dark-red. The mixture was brought to r.t., and the solvent was evaporated. The residue was extracted with 20 ml portions of pentane until the extract remained colorless (4 portions), and the combined extracts were concentrated. Column chromatography on silica gel (155 g) at -30°C with ether–pentane (3:1) furnished **6a** as a dark-red viscous oil (2.72 g, 61%). IR (film): $\nu = 2080$ (s), 1960 (s), 1900 (s), 1660 (m) cm^{-1}. ^{1}H-NMR(toluene-d_8, 400.1 MHz): $\delta =$ 0.75–1.45 (m, 14H, CHMe_2), 1.65 (s, 3H, Cp–Me), 2.50 (s, 3H, =CMe), 3.35 (br s, 3H, OMe), 4.25 and 4.40 (2s, 4H, C$_5$H$_4$). ^{13}C-NMR (CDCl$_3$): $\delta = 13.6$ (CpMe), 13.9 (SiCH), 17.0 and 17.1 (CHMe_2), 44.0 (C=N$_2$), 48.9 (=CMe), 52.0 (OMe), 87.0 and 88.0 (C-2,3,4,5, Cp), 104.2 (C-1, Cp), 168.5 (C=O, ester), 232.8 (CO, ligand), 339.6 (Mn=C). Anal. Calc. for C$_{19}$H$_{27}$MnN$_2$O$_5$Si (446.46): C, 51.12; H, 6.10. Found: C, 51.9; H, 6.30%.

Complexes **6b**–**d** were prepared analogously.

*4.6.1. Complex **6b***

BuLi in hexane was used; red–brown oil (2.30 g, 47%). IR (pentane): $\nu = 2080$ (s), 1970 (s), 1900 (s), 1685 (s) cm^{-1}. ^{1}H-NMR(toluene-d_8, 400.1 MHz): $\delta =$ 0.80–1.30 (m, 19H, CHMe_2, CH$_2$CH$_3$), 1.50 (t, 2H, CH$_2$), 1.65 (s, 3H, Cp–Me), 2.90 (t, 2H,=CCH$_2$), 3.35 (s, 3H, OMe), 4.30 and 4.47 (2 s, 4H, C$_5$H$_4$). ^{13}C-NMR (CDCl$_3$): $\delta = 12.6$ (CpMe), 13.8 (SiCH), 16.8 (CH$_2$$Me$), 17.0 and 17.1 (CH$Me_2$), 22.7 (CH$_2$), 31.0 (CH$_2$), 44.6 (C=N$_2$), 51.9 (OMe), 62.8 (=CCH$_2$), 86.9 and 87.8 (C-2,3,4,5, Cp), 104.5 (C-1, Cp), 168.5 (br, C=O, ester), 232.8 (CO, ligand), 346.6 (Mn=C).

*4.6.2. Complex **6c***

Phenyl lithium (2 M in cyclohexane–ether) was used; dark-red viscous oil (4.05 g, 80%). IR (film): $\nu = 2080$ (s), 1960 (s), 1880 (s), 1690 (s) cm^{-1}. ^{1}H-NMR (CDCl$_3$, 400.1 MHz, -20°C): $\delta = 0.97$–1.16 (m, 14H, CHMe_2), 1.88 (s, 3H, CpMe), 3.67 (s, 3H, OMe), 4.52 and 4.58 (2 s, 4H, C$_5$H$_4$), 6.87–6.93 (m, 2H), 7.18–7.24 (m$_c$, 1H), 7.25–7.30 (m$_c$, 2H). ^{13}C-NMR (CDCl$_3$, -20°C): $\delta =$ 13.2 (SiCH), 13.6 (CpMe), 16.7 and 17.5 (CHMe_2), 44.2 (br, C=N$_2$), 51.6 (OMe), 87.1 and 88.5 (C–2,3,4,5, Cp), 104.4 (C-1, Cp); 121.1, 126.8, 127.2, 156.2 (Ph); 168.5 (br, C=O, ester), 231.9 (CO, ligand), 334.0 (Mn=C). MS (CI, isobutane, 120 eV): $m/z = 509$ (47%) [MH^+], 508 (100) [M^+], 452 (45) [$M^+ - 2CO$], 424 (17) [$M^+ - 2CO - N_2$]. Anal. Calc. for $C_{24}H_{29}MnN_2O_5Si$ (508.53): C, 56.69, H, 5.75; N, 5.51. Found: C, 55.8; H, 5.80; N, 4.50%.

4.6.3. Complex **6d**

4-Methoxyphenyl lithium, prepared from 1-bromo-4-methoxybenzene and BuLi (see above), was used; red oil (3.72 g, 69%). IR (pentane): $\nu = 2100$ (s), 1960 (s), 1900 (s), 1680 (s) cm^{-1}. ^{13}C-NMR ($CDCl_3$): $\delta = 13.6$ (SiCH), 13.6 (Cp*Me*), 17.0 (CH*Me*$_2$), 44.8 ($C=N_2$), 51.7 (OMe), 55.1 (ArO*Me*), 87.4 and 88.3 (C-2,3,4,5, Cp), 104.2 (C-1, Cp); 111.8, 128.2, 149.9, 158.6 (Ph); 167.9 (C=O, ester), 232.2 (CO, ligand), 327.9 (Mn=C).

4.6.4. Complex **6e**

2-Furyl lithium, prepared from furan and BuLi (1.6 M in ether) was used; deep-red oil (1.15 g, 23%). IR (film): $\nu = 2080$ (s), 1940 (s), 1880 (sh), 1670 (m) cm^{-1}. ^{13}C-NMR ($CDCl_3$): $\delta = 12.8$ (SiCH), 13.6 (Cp*Me*), 16.9 (CH*Me*$_2$), 45.0 (br, $C=N_2$), 51.9 (OMe), 87.7 and 89.5 (C-2,3,4,5, Cp), 105.0 (C-1, Cp); 113.7, 119.7, 140.5, 164.0 (C-furyl); 169.0 (C=O, ester), 232.5 and 234.4 (CO, ligand), 348.3 (br, Mn=C). MS (CI, isobutane, 120 eV): $m/z = 499$ (100%) [MH^+], 498 (100) [M^+], 443 (26) [$MH^+ - 2CO$], 442 (45) [$M^+ - 2CO$], 415 (19) [$MH^+ - 2CO - N_2$], 414 (15) [$M^+ - 2CO - N_2$].

4.6.5. Complex **6f**

1-Methylpyrrol-2-yl lithium, prepared from 1-methylpyrrole and BuLi (1.6 M in ether) was used; deep-red oil (3.68 g, 72%). IR (film): $\nu = 2080$ (s), 1960 (s), 1880 (s), 1670 (m) cm^{-1}. ^{13}C-NMR ($CDCl_3$): $\delta =$ 12.8 (SiCH), 13.7 (Cp*Me*), 16.9 and 17.1 (CH*Me*$_2$), 34.0 (NMe), 44.5 ($C=N_2$), 51.6 (OMe), 88.1 and 88.4 (C-2,3,4,5, Cp), 104.7 (C-1, Cp); 106.0, 107.5, 121.5, 148.7 (C-pyrrolyl); 169.4 (C=O, ester), 232.0 and 232.2 (CO, ligand), 324.3 (Mn=C).

4.7. *Dicarbonyl{1-ethoxy-2-[(1-diazo-2-methoxy-2-oxoethyl)diisopropylsilyl]ethylidene}-(η^5-methylcyclopentadienyl)manganese* **(8a)**

A solution of **7a** [6] (1.59 g, 6.05 mmol) in ether (20 ml) was cooled at −78°C and BuLi (1.6 M solution in hexane, 3.8 ml, 6.08 mol) was added during 30 min. The mixture was brought to −40°C, and **1** (6.05 mmol) in pentane (10 ml) was added dropwise. The dark-red mixture was allowed to warm to 0°C within 2 h, the solvent was evaporated, and the residue was subjected to column chromatography at −30°C [silica gel (150 g), pentane-ether (9:1)] to give **8a** (1.23 g, 43%) as a deep-red oil. IR (pentane): $\nu = 2080$ (s), 1940 (s), 1875 (s), 1675 (s) cm^{-1}. ^{1}H-NMR (toluene-d_8, 400.1 MHz): $\delta = 0.80{-}1.30$ (m, 14H, CH*Me*$_2$), 1.55 (m$_c$, 3H, OCH$_2$*Me*), 1.70 (s, 3H, *Me*Cp), 3.10 (s, 2H, $=CCH_2$), 3.36 (s, 3H, OMe), 4.30 (m, 2H, OCH$_2$), 4.27 and 4.55 (2 s, 2 × 2H, C_5H_4). ^{13}C-NMR (toluene-d_8): $\delta = 12.8$ (*C*HMe$_2$), 13.6 (*Me*Cp), 14.9 (OCH$_2$*Me*), 18.2 (CH*Me*$_2$), 41.9 (CN_2), 48.6 (=C*C*H$_2$), 51.4 (OMe), 72.2 (OCH$_2$), 86.5 and 88.3 (C-2,5 and C-3,4 of Me*Cp*), 103.7 (C-1 of Me*Cp*), 168.8 (COO), 234.0 (CO), 337.9 (Mn=C). Anal. Calc. for $C_{21}H_{31}MnN_2O_5Si$ (474.53): C, 53.15; H, 6.58; N, 5.90. Found: C, 54.7, H, 6.5; N, 4.0%.

4.8. *Dicarbonyl(methylcyclopentadienyl)-(1-ethoxy-1-butylidene)manganese* **(7b)**

This compound was prepared from tricarbonyl-(methylcyclopentadienyl)manganese and BuLi by analogy to literature [6]; red oil, yield: 60%. ^{1}H-NMR ($CDCl_3$, 400.1 MHz): $\delta = 0.90$ (t, 3H, CH$_2$CH$_2$*Me*), 1.30 (m$_c$, 2H, CH$_2$), 1.42 (m$_c$, 2H, CH$_2$), 1.47 (t, 3H, OCH$_2$*Me*), 1.93 (s, 3H, Cp*Me*), 2.92 (t, 2H,=CCH$_2$), 4.62 (q, 2 H, OCH$_2$), 4.53 and 4.71 (2 s, 2 × 2H, C_5H_4). ^{13}C-NMR ($CDCl_3$): $\delta = 13.6$, 14.1, 14.5, 22.8, 31.7, 59.6, 72.2, 85.9, 86.8, 103.0, 233.4, 342.5.

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References

[1] M. Regitz (Ed.), Methoden der organischen Chemie (Houben-Weyl), vol. E19b, Thieme, Stuttgart, 1989.

[2] (a) G. Maas, Topics Curr. Chem. 137 (1987) 77. (b) T. Ye, M.A. McKervey, Chem. Rev. 94 (1994) 1091. (c) M.P. Doyle, M.A. McKervey, T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides, Wiley, New York, 1998.

[3] (a) E.O. Fischer, A. Maasböl, Angew. Chem. 76 (1964) 645. (b) E.O. Fischer, A. Maasböl, Angew. Chem. Int. Ed. Engl. 3 (1964) 580. (c) E.O. Fischer, Angew. Chem. 86 (1974) 651.

[4] (a) K.H. Dötz, Angew. Chem. 96 (1984) 573. (b) K.H. Dötz, Angew. Chem. Int. Ed. Engl 23 (1984) 587. (c) W.D. Wulff, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991, p. 1065. (d) M. Brookhart, W.B. Studabaker, Chem. Rev. 87 (1987) 411. (e) D.F. Harvey, M.F. Brown, Tetrahedron Lett. 21 (1990) 529. (f) B.C. Söderberg, L.S. Hegedus, Organometallics (1990) 3113. (g) A. Wienand, H.-U. Reissig, Organometallics 9 (1990) 3133. (h) M. Buchert, H.-U. Reissig, Chem. Ber. 125 (1992) 2723. (i) J. Pfeiffer, K.H. Dötz, Angew. Chem. 109 (1997) 2948. (j) J. Pfeiffer, K.H. Dötz, Angew. Chem. Int. Ed. Engl. 36 (1997) 2828.

[5] A preliminary report of part of this work has appeared: D. Mayer, G. Maas, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry II, VCH, Weinheim, 1996, p. 565.

[6] (a) E.O. Fischer, A. Maasböl, Chem. Ber. 100 (1967) 2445. (b) R. Aumann, E.O. Fischer, Chem. Ber. 101 (1968) 954.

[7] E.O. Fischer, T. Selmayr, F.R. Kreißl, U. Schubert, Chem. Ber. 110 (1977) 2574.

[8] A. Fronda, F. Krebs, B. Daucher, T. Werle, G. Maas, J. Organomet. Chem. 424 (1992) 253.

[9] K.H. Dötz, H. Larbig, J. Organomet. Chem. 433 (1992) 115.

[10] M.F. Gross, M.G. Finn, J. Am. Chem. Soc. 116 (1994) 10921.

[11] U. Schubert, J. Organomet. Chem. 358 (1988) 215.

[12] (a) C.P. Casey, S.H. Bertz, T.J. Burkhardt, Tetrahedron Lett. (1973) 1421. (b) M.P. Doyle, J.H. Griffin, J. da Conceição, J. Chem. Soc. Chem. Commun. (1985) 328.

[13] (a) U. Schubert, Organometallics 1 (1982) 1085. (b) U. Kirchgässner, H. Piana, U. Schubert, J. Am. Chem. Soc. 113 (1991) 2228.

[14] (a) P.M. Treichel, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon Press, Oxford, 1982, p. 129. (b) B.L. Balzer, M. Cazanoue, M. Sabat, M.G. Finn, Organometallics 11 (1992) 1759.

[15] M.J. McGeary, J.L. Templeton, J. Organomet. Chem. 323 (1987) 199.

[16] C.S. Yi, G.L. Geoffroy, C.A. White, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 3806.

[17] Y. Yu, J. Chen, X. Wang, Q. Wu, Q. Liu, J. Organomet. Chem. 516 (1996) 81.

[18] (a) C.G. Kreiter, Angew. Chem. 80 (1968) 402. (b) C.G. Kreiter, Angew. Chem. Int. Ed. Engl. 7 (1968) 390. (c) C.P. Casey, R.A. Boggs, R.L. Anderson, J. Am. Chem. Soc. 94 (1972) 8947. (d) C.P. Casey, W.R. Brunsvold, J. Organomet. Chem. 118 (1976) 309.

[19] H.-O. Kalinowski, S. Berger, S. Braun, ^{13}C-NMR Spektroskopie, Thieme, Stuttgart, 1984, p. 446.