ORGANOMETALLICS

A (.eta.1-iminoacyl)zirconocene complex formed by alkyl isocyanide insertion into the metal-to-carbon bond of (.eta.2-formaldehyde)zirconocene

Gerhard. Erker, Miguel. Mena, Carl. Krueger, and Ralf. Noe

Organometallics, **1991**, 10 (4), 1201-1203• DOI: 10.1021/om00050a064 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

A (η^1-Iminoacyl)zirconocene Complex Formed by Alkyl Isocyanide Insertion into the Metal to Carbon Bond of (η^2-Formaldehyde)zirconocene

Gerhard Erker* and Miguel Mena†

Institut für Organische Chemie der Universität Münster, Orléans-Ring 23, D-4400 Münster, FRG

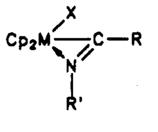
Carl Krüger and Ralf Noe

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a. d. Ruhr, FRG

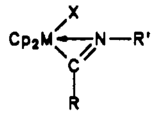
Received May 24, 1990

Summary: The (η^2-formaldehyde)zirconocene complex $(Cp_2ZrOCH_2)_2$ (**1**) reacts with alkyl isocyanides CN-R (**2a-c**) (R = $-CH_2SiMe_3$, $-CH_2CMe_3$, $-CMe_2CH_2CMe_3$) to give the insertion products $[Cp_2ZrOCH_2C(=NR)]_2$ (**3a-c**). The doubly oxygen bridged C_{2h}-symmetric metallatricyclic complexes **3** contain (η^1-iminoacyl)zirconocene moieties. The (trimethylsilyl)methyl isocyanide insertion product **3a** was characterized by X-ray diffraction. It crystallizes in space group $P\bar{1}$ with cell parameters a = 7.977 (1) Å, b = 10.162 (1) Å, c = 11.753 (1) Å, α = 64.53 (1)°, β = 85.27 (1)°, γ = 79.89 (1)°, Z = 1, R = 0.024, and R_w = 0.035. The C=N bond length in **3a** is 1.274 (2) Å; the Zr-C distance of the (η^1-iminoacyl)zirconocene moiety is 2.374 (1) Å.

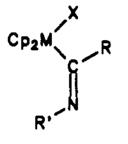
Group 4 metallocene complexes of the general type $Cp_2M(X)(-CR_nY)$ with Y having π-donor properties [e.g. $-CR_nY$ being acyl ($-CR=O$), iminoacyl ($-CR=NR'$), phosphinomethyl ($-CH_2PR_2$), or alkoxymethyl ($-CH_2OR$)] are known to adopt either one of two possible η^2-bonding modes ("Y-outside" A, "Y-inside" B) or a "η^1-Y-outside" type structure (C). Calculations have shown that for most ligand types $-CR_nY$ the structural situations A-C correspond to local minima on the hypersurface;[1] η^2-type structures have been verified by experiment to be the global minima for numerous examples of acyl- or iminoacyl-Cp_2M and related complexes.[2] We have now found a stable (η^1-iminoacyl)zirconocene complex, for which the η^1- to η^2-R'N=CR[Zr] rearrangement is precluded by incorporation of the functional group into a small metallacyclic ring system.[3]



η^2-N-outside (A)



η^2-N-inside (B)



η^1-N-outside (C)

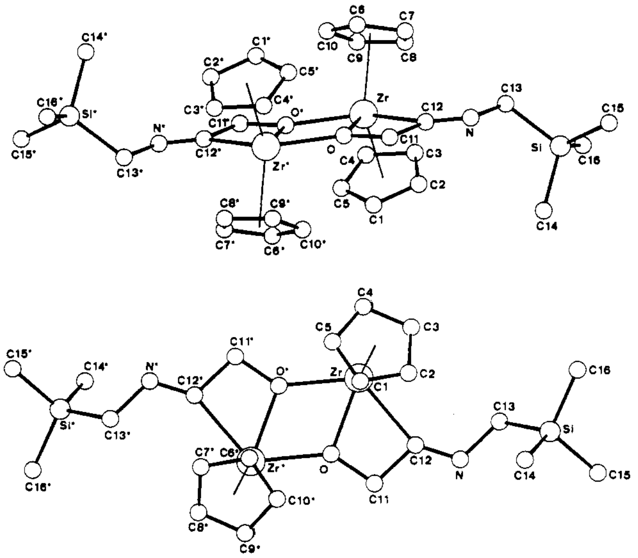


Figure 1. Two projections of the molecular structure of the (η^1-iminoacyl)zirconocene complex **3a**.

Table I. Bond Distances (Å) and Angles (deg) of 3a

Zr-C(1)	2.540 (2)	Zr-C(10)	2.538 (2)
Zr-C(2)	2.539 (2)	Zr-C(12)	2.374 (1)
Zr-C(3)	2.515 (2)	Zr-O	2.194 (1)
Zr-C(4)	2.516 (2)	Zr-O*	2.175 (1)
Zr-C(5)	2.534 (2)	O-C(11)	1.423 (2)
Zr-C(6)	2.542 (2)	N-C(12)	1.274 (2)
Zr-C(7)	2.550 (2)	N-C(13)	1.473 (2)
Zr-C(8)	2.529 (2)	C(11)-C(12)	1.518 (2)
Zr-C(9)	2.531 (2)		
O*-Zr-O	64.8 (1)	C(13)-N-C(12)	117.9 (1)
C(12)-Zr-O	59.9 (1)	C(12)-C(11)-O	102.1 (1)
C(12)-Zr-O*	124.7 (1)	C(11)-C(12)-N	118.6 (1)
Zr*-O-Zr	115.2 (1)	C(11)-C(12)-Zr	93.6 (1)
C(11)-O-Zr	104.4 (1)	N-C(12)-Zr	147.8 (1)
C(11)-O-Zr*	140.4 (1)	N-C(13)-Si	113.6 (1)

Starting material for our synthesis is (η^2-formaldehyde)zirconocene (**1**), prepared by hydrozirconation of carbon monoxide followed by removal of Cp_2ZrCl_2 by means of treatment with 2 equiv of methyllithium, as previously described.[4] The complex (η^2-CH_2O)$ZrCp_2$ is isolated as a doubly O-Zr bridged dimer **1** [^{1}H NMR (benzene-d_6): δ 2.42. ^{13}C NMR (benzene-d_6): δ 64.0 ($^1J_{CH}$ = 153 Hz, CH_2)]. According to the X-ray crystal structure analysis, the $ZrOCH_2$ moiety in **1** has a pronounced metallaoxirane character [d(C(1)-Zr) = 2.243 (3) Å, d(C(1)-O) = 1.395 (4) Å].[4]

The (η^2-formaldehyde)zirconocene dimer **1** reacts with alkyl isocyanides CN-R (**2a-c**) (R = CH_2SiMe_3, CH_2CMe_3, $CMe_2CH_2CMe_3$) at room temperature to give the C_{2h}-symmetric insertion products **3a-c**. Complex **3a** (R = CH_2SiMe_3) exhibits an IR ν(C=N) band at 1596 cm^{-1} and a ^{13}C NMR ($CDCl_3$, 50 MHz) imino carbon resonance at

---

† Present address: Departamento de Quimica Inorganica, Alcala de Henares, Madrid, Spain.

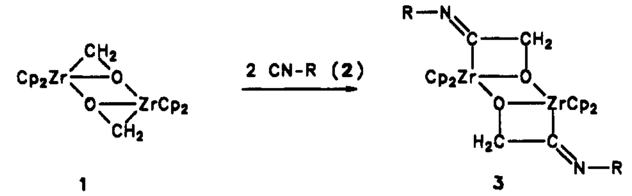
(1) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. Hofmann, P.; Stauffert, P.; Tatsumi, K.; Nakamura, A.; Hoffmann, R. *Organometallics* **1985**, *4*, 404.

(2) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(3) We have recently shown that $Cp_2ZrCl(CH_2OCH_3)$ exhibits a "η^2-O-inside" (B) type structure, whereas $Cp_2TiCl(CH_2OCH_3)$ is of the "η^1-O-outside" type (C) in the crystal: Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251. Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403. Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *338*, C4. Erker, G.; Schlund, R.; Albrecht, M.; Sarter, C. *J. Organomet. Chem.* **1988**, *353*, C27.

(4) Erker, G.; Hoffmann, U.; Zwettler, R.; Betz, P.; Krüger, C. *Angew. Chem.* **1989**, *101*, 644; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630. Erker, G. *Angew. Chem.* **1989**, *101*, 411; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397. Erker, G.; Hoffmann, U.; Zwettler, R.; Krüger, C. *J. Organomet. Chem.* **1989**, *367*, C15.

0276-7333/91/2310-1201$02.50/0



R = $-CH_2-SiMe_3$ (a), $-CH_2-CMe_3$ (b), $-CMe_2-CH_2-CMe_3$ (c)

δ 220.2. Both values are probably typical of (η^1-iminoacyl)zirconocene complexes but are only slightly out of the range of δ(*C*=N) and ν(C=N) values as reported for many (η^2-iminoacyl)zirconium complexes.[2] The ring CH_2 group in **3a** shows NMR signals at δ 88.3 (^{13}C, $^1J_{CH}$ = 140 Hz) and δ 4.67 (^1H). Remarkably, the latter resonance exhibits a rather strong coupling with the nitrogen-bound $-CH_2SiMe_3$ protons at δ 2.99 ($^5J_{HH}$ = 1.6 Hz). Complexes **3b,c** show similar spectroscopic features.

Complex **3a** was characterized by an X-ray crystal structure analysis. It has revealed that both metallacyclic Zr–C bonds of the binuclear (formaldehyde)zirconocene starting material have undergone insertion of the $CN-CH_2SiMe_3$ reagent and the dimeric metallatricyclic structure has been retained. Ring enlargement of the $ZrOCH_2$ three-membered rings has led to the formation of two symmetry-equivalent planar four-membered metallacycles [the sum of the bonding angles O–Zr–C(12) (59.9 (1)°), Zr–C(12)–C(11) (93.6 (1)°), C(12)–C(11)–O (102.1 (1)°), and C(11)–O–Zr (104.4 (1)°) is 360.0°].

The iminoacyl functional group is clearly η^1-bonded to zirconium [angle C(12)–N–C(13) 117.9 (1)°, bond distances Zr–C(12) 2.374 (1) Å, C(12)–N 1.274 (2) Å]. While the metal to carbon bond in (η^1-iminoacyl)zirconocene **3a** is longer than typically found in (η^2-iminoacyl)zirconocene complexes (range 2.21–2.25 Å),[2] there seems to be no differentiation in the C=N distances between the two isomeric iminoacyl coordination modes [C=N bond lengths in (η^2-iminoacyl)zirconium complexes have been reported to range from 1.26 to 1.29 Å].[2]

The four-membered $Cp_2ZrOCH_2C(=NR)$ metallacycles are coupled via bridging O–Zr bonds. The central Zr_2O_2 ring of **3a** is planar [angles O–Zr–O* 64.8 (1)°, Zr–O–Zr* 115.2 (1)°]. The sum of bonding angles around the tricoordinate oxygens is 360° [Zr–O–Zr* 115.2 (1)°, Zr–O–C(11) 104.4 (1)°, Zr*–O–C(11) 140.4 (1)°]. Thus, the central framework of complex **3a** is oriented coplanar. Actually, coplanarity extends as far as to the peripheral N and C(13) (and their symmetry equivalents). Only the Cp ring systems, the $-SiMe_3$ substituents at C(13), and hydrogen atoms at C(11) are oriented away from the central major plane of complex **3a**. The angle between the normals to the η-cyclopentadienyl rings at Zr is 126.2°. Distances to the midpoints amount to 2.24 and 2.25 Å, respectively.

It is interesting to note that the zirconium to oxygen bonds in **3a** connecting the four-membered metallacyclic mononuclear subunits are markedly shorter at *d*(Zr–O*) = 2.175 (1) Å than the Zr–O bonds (2.194 (1) Å) inside the lateral metallacycles. This is contrary to what is usually observed for many similar types of oxygen-bridged Cp_2MOX dimers.[5] Probably, the electron-withdrawing properties of the η^1-iminoacyl functionality leads to an increased electrophilicity of the zirconium center in the metallaoxetane unit of **3a**.

Table II. Atomic Coordinates of 3a

atom	*x*	*y*	*z*
Zr	0.0387 (1)	0.0599 (1)	0.1217 (1)
Si	−0.4497 (1)	0.3400 (1)	0.3330 (1)
O	−0.1465 (1)	0.0151 (1)	0.0202 (1)
N	−0.3709 (2)	0.1189 (2)	0.2438 (1)
C(1)	−0.0087 (3)	0.3248 (2)	−0.0447 (2)
C(2)	−0.0569 (3)	0.3317 (2)	0.0679 (2)
C(3)	0.0871 (3)	0.2869 (2)	0.1419 (2)
C(4)	0.2254 (2)	0.2535 (2)	0.0722 (3)
C(5)	0.1620 (3)	0.2788 (2)	−0.0433 (2)
C(6)	0.0625 (4)	−0.2042 (2)	0.2896 (2)
C(7)	0.0051 (3)	−0.1173 (2)	0.3520 (2)
C(8)	0.1294 (3)	−0.0400 (2)	0.3485 (2)
C(9)	0.2701 (3)	−0.0776 (3)	0.2847 (2)
C(10)	0.2272 (4)	−0.1819 (3)	0.2483 (2)
C(11)	−0.3067 (2)	0.0469 (2)	0.0733 (2)
C(12)	−0.2555 (2)	0.0895 (2)	0.1729 (1)
C(13)	−0.3198 (2)	0.1633 (2)	0.3381 (2)
C(14)	−0.5176 (3)	0.4706 (2)	0.1693 (2)
C(15)	−0.6421 (3)	0.2931 (3)	0.4351 (2)
C(16)	−0.3151 (3)	0.4288 (3)	0.3930 (2)

Experimental Section

All reactions were carried out under argon by using Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. For additional general information, including a list of spectrometers used, see ref 6. The (η^2-formaldehyde)zirconocene dimer 1 was prepared as previously described.[4]

Reaction of 1 with $CN-CH_2SiMe_3$. To a suspension of 410 mg (0.82 mmol) of 1 in 20 mL of toluene was added with stirring 0.23 mL (1.63 mmol) of (trimethylsilyl)methyl isocyanide (**2a**) at ambient temperature. The resulting orange suspension was stirred overnight at 40 °C. From the reaction mixture a colorless solid precipitated at room temperature, which was collected by filtration. Cooling of the filtrate to −30 °C gave additional product. The combined precipitates were washed with pentane and dried in vacuo. Total yield of **3a**: 0.50 g (84%). Mp: 233 °C (DTA) dec. Anal. Calcd for $C_{32}H_{46}N_2O_2Si_2Zr_2$ (729.3): C, 52.70; H, 6.36; N, 3.84. Found: C, 52.55; H, 6.66; N, 3.81. IR (KBr): ν(C=N) 1596 cm^{-1}. MS (70 eV, EI): m/z = 726 (1%, M^+), 613 (5, $M^+ - CNCH_2SiMe_3$), 583 (2), 500 (28), 470 (40), 390 (19), 220 (43), 73 (100). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.01 (s, 20 H, Cp), 4.67 (t, $^5J_{HH}$ = 1.6 Hz, 4 H, $ZrOCH_2$), 2.99 (t, $^5J_{HH}$ = 1.6 Hz, 4 H, NCH_2), 0.16 (s, 18 H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 220.2 (C=N), 108.8 ($^1J_{CH}$ = 172 Hz, Cp), 88.3 ($^1J_{CH}$ = 140 Hz, $ZrOCH_2$), 51.0 ($^1J_{CH}$ = 123 Hz, NCH_2Si), −1.9 ($^1J_{CH}$ = 119 Hz, $Si(CH_3)_3$). X-ray crystal structure analysis of **3a**: $C_{32}H_{46}N_2O_2Si_2Zr_2$, MW = 729.3, space group $P\bar{1}$, a = 7.977 (1) Å, b = 10.162 (1) Å, c = 11.753 (1) Å, α = 64.53 (1)°, β = 85.27 (1)°, γ = 79.89 (1)°, V = 846.8 $Å^3$, d_{calc} = 1.43 g cm^{-3}, μ = 7.03 cm^{-1}, Z = 1, λ = 0.710 69 Å, measured reflections 4930 ($\pm h,\pm k,+l$), $(\sin\theta)/\lambda_{max}$ = 0.70, 4727 observed reflections ($I > 2\sigma(I)$), 181 refined parameters, R = 0.024, R_w = 0.035, ρ_{max} = 0.55 e/$Å^3$. The structure was solved by the heavy-atom method, and hydrogen atom positions were calculated and kept fixed in the final refinement.

Reaction of 1 with $CN-CH_2C(CH_3)_2$. Complex 1 (0.50 g, 0.99 mmol) was suspended in 40 mL of toluene. Neopentyl isocyanide (**2b**) (0.19 g, 1.99 mmol) was added at room temperature with stirring. After 20 min, an orange solution was obtained. The reaction mixture was heated at 50 °C overnight with stirring. Cooling to room temperature gave **3b** as a white solid. A second product fraction was obtained from the filtrate at −30 °C. Combined yield of **3b**: 0.60 g (86%). Mp: 248 °C dec. Anal. Calcd for $C_{34}H_{46}N_2O_2Zr_2$ (697.2): C, 58.57; H, 6.65; N, 4.02. Found: C, 58.48; H, 6.92; N, 4.13. IR (KBr): ν(C=N) 1620, 1608 cm^{-1}. MS (70 eV, EI): m/z = 694 (0.1%, M^+), 597 (2, $M^+ - CNCH_2CMe_3$), 567 (3), 500 (19), 470 (63), 390 (26), 220 (43), 57 (100). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.08 (s, 20 H, Cp), 4.78 (t, $^5J_{HH}$ = 1.6 Hz, $ZrOCH_2$), 3.07 (t, $^5J_{HH}$ = 1.6 Hz, NCH_2), 1.13 (s, 18 H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 223.8 (C=N), 108.8 ($^1J_{CH}$ = 172 Hz, Cp), 88.6 ($^1J_{CH}$ = 140 Hz, $ZrOCH_2$), 70.1 ($^1J_{CH}$ = 129 Hz, NCH_2), 32.3 (CMe_3), 28.4 ($^1J_{CH}$ = 125 Hz, $C(CH_3)_3$).

---

(5) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668 and references cited therein.

(6) Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349.

Reaction of 1 with $CNC(CH_3)_2CH_2C(CH_3)_3$. To a suspension of 0.52 g (1.03 mmol) of 1 in 30 mL of toluene was added 0.38 mL (2.16 mmol) of 1,1,3,3-tetramethylbutyl isocyanide (**2c**) at room temperature with stirring. After 1 h, a clear yellow solution was obtained, which was concentrated to 15 mL and cooled to -30 °C to give 0.65 g (82%) of **3c** as slightly yellow needles, mp 160 °C (DTA) dec. Anal. Calcd for $C_{40}H_{58}N_2O_2Zr_2$ (781.4): C, 61.49; H, 7.48; N, 3.59. Found: C, 61.78; H, 7.56; N, 3.60. IR (KBr): ν(C=N) 1621 cm^{-1}. MS (70 eV, EI): m/z = 778 (1%, M^+), 500 (3), 470 (35), 390 (15), 220 (16), 57 (100). ^1H NMR (benzene-d_6, 200 MHz): δ 5.86 (s, 20 H, Cp), 5.02 (s, 4 H, $ZrOCH_2$), 1.83 (s, 4 H, CCH_2C), 1.29 (s, 12 H, $C(CH_3)_2$), 1.26 (s, 18 H, $C(CH_3)_3$). ^{13}C NMR (benzene-d_6, 50 MHz): δ 215.9 (C=N), 110.3 ($^1J_{CH}$ = 172 Hz, Cp), 85.1 ($^1J_{CH}$ = 139 Hz, $ZrOCH_2$), 64.2 ($NCMe_2$), 57.8 ($^1J_{CH}$ = 124 Hz, CCH_2C), 32.4 (CMe_3), 32.4 ($^1J_{CH}$ = 125 Hz, $C(CH_3)_2$), 30.2 ($^1J_{CH}$ = 124 Hz, $C(CH_3)_3$).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged. M.M. thanks the Ministerio de Educacion y Ciencia, Madrid, and the Alexander von Humboldt-Stiftung for a fellowship.

Registry No. 1, 88385-20-0; **2a**, 30718-17-3; **2b**, 72443-18-6; **2c**, 14542-93-9; **3a**, 132776-60-4; **3b**, 132776-62-6; **3c**, 132776-61-5.

Supplementary Material Available: For **3a**, tables of detailed information on the crystal structure determination, final atomic position parameters, final thermal parameters, and interatomic distances and angles (7 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Synthesis of Alkoxymethyl Complexes from Metal Formyls

Dorothy H. Gibson,* Kathryn Owens, Santosh K. Mandal, William E. Sattich, and Jaime O. Franco

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

Received July 23, 1990

Summary: Syntheses of seven alkoxymethyl complexes, $M-CH_2OR$ (R = Me, Et), from the corresponding metal formyls are described; the metals are manganese (compounds **1a-b**, **2**, and **3**), rhenium (compounds **4** and **5**), or molybdenum (compound **6**). Four of these (**1b** and **3-5**) are new compounds; the details of the syntheses of the other three have not been reported previously. Examples are given of three distinct synthetic routes; all routes require initiation by the action of an electrophile on the metal formyl complex. Variations in the procedures are dictated by the reactivity of the formyl complex and that of its protonated or alkylated form.

Table I. Summary of Synthetic Methods for Alkoxymethyl Complexes

compd	synth method	prod yield, %[a]/reacn time
cis-$Mn(CO)_4PPh_3(CH_2OCH_3)$ (**1a**)	A	84/15 min
cis-$Mn(CO)_4PPh_3(CH_2OCH_2CH_3)$ (**1b**)	A	68/15 min
mer,trans-$Mn(CO)_3(PPh_3)_2(CH_2OCH_3)$ (**2**)	B	78/14 h
same	C	86[b]/10 min
mer,trans-$Mn(CO)_3[P(OPh)_3]_2(CH_2OCH_3)$ (**3**)	B	80/3 h
mer,trans-$Re(CO)_3(PPh_3)_2(CH_2OCH_3)$ (**4**)	C	89/20 min
same	C	86[b]/15 min
mer,trans-$Re(CO)_3[P(OPh)_3]_2(CH_2OCH_3)$ (**5**)	B	61/30 min
cis- and *trans*-$CpMo(CO)_2[P(OPh_3)]CH_2OCH_3$ (**6**)	A	63/5 min

[a] Product yields are based on reaction stoichiometry. [b] The isolated carbene complex was used; the overall time and yield from the formyl complex are reported.

Alkoxymethyl complexes are useful precursors to carbene complexes[1] and several other types of C_1 ligands to transition metals.[2] A variety of methods have been reported for their synthesis: (1) by reaction of a metal anion with a halomethyl ether,[3] (2) by nucleophilic substitution on a halomethyl complex by an alcohol or an alkoxide,[4] (3) by reduction of a secondary alkoxycarbene complex,[5] (4) by alkylation of a cationic η^2-formaldehyde complex,[6] (5) by oxidative addition of a halomethyl ether to a coordinatively unsaturated complex,[7] (6) by hydride abstraction from a methyl complex followed by alkoxide addition,[8] (7) by decarbonylation of an alkoxyacetyl complex,[9] (8) by reduction of a metal carbonyl cation in the presence of an alcohol,[10] and (9) by reaction of a hydroxymethyl complex with an alcohol.[11] In addition to method 1, several others depend, indirectly, on the availability of a metal anion. Methods 1 and 2 are the ones which have been most commonly used. Although effective, method 1 is objectionable because of the toxicity of halomethyl ethers.

The present work includes method 3 but details examples of three distinct routes to alkoxymethyl complexes from neutral metal formyl complexes. All three routes utilize an electrophile to initiate further transformation of the formyl complex;[12] the choice of method is dictated by the reactivity of the substrate and that of its protonated

---

(1) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

(2) (a) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604. (b) Markham, J.; Tolman, W.; Menard, K.; Cutler, A. *J. Organomet. Chem.* **1985**, *294*, 45.

(3) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508.

(4) Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7.

(5) (a) Bodnar, T.; LaCroce, S. J.; Cutler, A. *J. Am. Chem. Soc.* **1980**, *102*, 3292. (b) Wong, W.-K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440.

(6) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503.

(7) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

(8) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(9) Sisak, A.; Sampar-Szerencses, E.; Galamb, V.; Nemeth, L.; Ungvary, F.; Palyi, G. *Organometallics* **1989**, *8*, 1096.

(10) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

(11) (a) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. (b) Nelson, G. O. *Organometallics* **1983**, *2*, 1474. (c) Nelson, G. O.; Sumner, C. E. *Organometallics* **1986**, *5*, 1983.

(12) For the preparations of the formyl complexes used in this work, see Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.

0276-7333/91/2310-1203$02.50/0