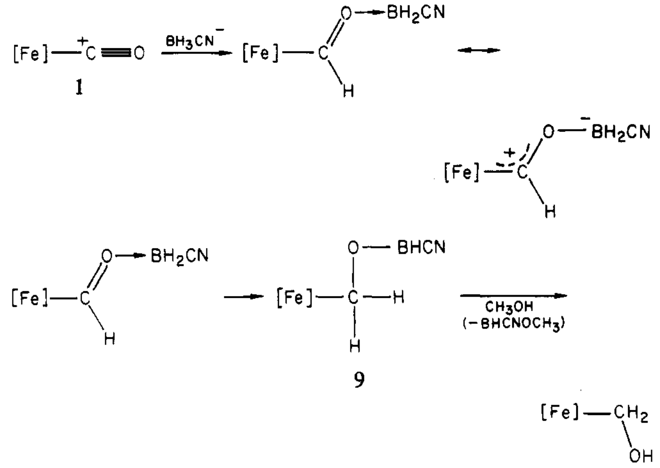
formyl complex[2a–d] $CpFe(CO)_2CHO$ (**8**)[16] or CH_2O deinsertion from **2** would account for **5**.

So why does the alcoholic $NaBH_3CN$ medium selectively reduce **1**[17] to **2** and **3a,b**? $NaBH_3CN$ serves as an excellent reducing agent for Lewis acids[18a] and is both milder and more selective than BH_4^- or Et_3BH^- toward coordinated ligands.[18b] A plausible reaction scheme for reduction of **1** thus incorporates Lewis acid stabilization and subsequent reduction of the formyl complex **8**[16] by BH_2CN,[19] giving **9**. A similar scheme was proposed for the BH_3 reduction of $CpFe(CO)_2COCH_3$ to $CpFe(CO)_2CH_2CH_3$ via a more reactive alkoxyborane intermediate $CpFe(CO)_2CH(OBH_2)CH_3$.[20] Transesterification of **9** by methanol then affords **2**.



One of the CO ligands on $CpFe(CO)_3^+$ (**1**) can be incorporated by treating the appropriate $CpFe(CO)_2$ reagent with CO or CO_2. Carbonylation of halide complexes $CpFe(CO)_2X$,[14,21a] labile salts $CpFe(CO)_2L^+$ (L = acetone,[21b] isobutylene,[21c] H_2O[21d]), or even ferrocene[21e] accordingly represent established preparative procedures of **1**. We now report that protonation of the CO_2 adduct of $CpFe(CO)_2^-Na^+$[22] gives **1** in high yield; presumably an acid labile $CpFe(CO)_2CO_2H$[23] precursor is involved. (Alkoxycarbonyl complexes, e.g., $CpFe(CO)_2CO_2Et$, exhibit similar acid lability.[8]) The exact nature of the CO_2 adduct of $CpFe(CO)_2^-$ remains obscure (studies are in progress), but the formulation $CpFe(CO)_2C(O)OCO_2^-$ is consonant with facile generation of Na_2CO_3 in the absence of acid.[22] A similar $(CO_2)_2$ adduct of $W(CO)_5^{2-}$ also decomposes to CO_3^{2-} and $W(CO)_6$;[24] and other examples exist for both alkylation of ligated CO_2, giving an alkoxycarbonyl complex,[25a] and reduction to CO complexes.[25b] This study documents the first example of ligated CO_2 fixation, via a CO complex, to a transition-metal alkyl complex.

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Registry No. **1**, 31781-41-6; **3a**, 12108-35-9; **3b**, 12244-98-3; **4a**, 80293-89-6; **4b**, 80288-46-6; **5**, 35913-82-7; $CpFe(CO)_2^-Na^+$, 12152-20-4; $[CpFe(CO)_2]_2$, 12154-95-9; $NaBH_3CN$, 25895-60-7; methanol, 67-56-1; ethanol, 64-17-5; CO_2, 124-38-9; phenyl isocyanate, 103-71-9; ethyl isocyanate, 109-90-0.

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(17) (a) Our results with the $NaBH_3CN$ reduction of **1** are not prototypal for other cationic metal carbonyl complexes. Both $CpFe(CO)_2PPh_3^+$ and $CpMo(CO)_3PPh_3^+$ undergo no reaction with $NaBH_3CN$ in CH_3OH (12 h), but refluxing the solutions for 12 h provided cyano complexes: $CpFe(CO)PPh_3(CN)$[17b] (42% conversion, 41% $CpFe(CO)_2PPh_3^+BF_4^-$ recovered) and $CpMo(CO)_2PPh_3(CN)$[17c] (18% yield, 44% $CpMo(CO)_2PPh_3(H)$ also obtained). $CpMo(CO)_4^+$, $Mn(CO)_6^+$, and $Mn(CO)_5PPh_3^+$ (all PF_6^-) reacted with 1 equiv of $NaBH_3CN$ in CH_3OH (0 °C, 1 h) and exclusively gave the corresponding neutral hydride complexes in 80–95% yields. $Co(CO)_4PPh_3^+PF_6^-$ converted to $[Co(CO)_3PPh_3]_2$ quantitatively under the same conditions. (b) Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660. Faller, J. W. *J. Organomet. Chem.* **1975**, *96*, 99. (c) Beach, D. L.; Dattilo, M.; Barnett, K. W. *Ibid.* **1977**, *140*, 47.

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Convenient Route to Monocyclopentadienylzirconium(IV) Complexes

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Monocyclopentadienyl complexes have substantially contributed to the diversity of features of organometallic transition–metal compounds. However, surprisingly few such substrates have been described for group 4B metals. A major cause for the rare occurrence of $CpMR_3$ examples for at least the elements Zr and Hf appears to be the lack of easily available precursors rather than an extraordinarily low stability.[1] We and others[2a] have noticed that a suitable starting material such as $CpZrCl_3$ (**3**) for a synthesis of previously undisclosed substrates $CpZr(aryl)_3$ (**5**) is difficult to obtain by the usual *nucleophilic* routes via substitution of halide by cyclopentadienyl anion from various sources.[3] Sufficiently pure samples of **3** have recently been obtained in small quantities by two different *radical* pathways.[2] We here report an easily performable new synthesis of **3** which, in our opinion, appears to be superior to the tedious procedures reported yielding this versatile starting material in large amounts and high purity.

The photoinduced chlorination of zirconocene dichloride **1** leads to the selective removal of only one cyclopentadienyl ligand when carried out at ambient temperature.[4] Presumably

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the reaction is initiated by photochemical formation of transient $CpZrCl_2$ (**2a**) which starts the observed very efficient radical chain reaction being consumed by molecular chlorine to form **3** and a chain carrying Cl radical. $CpZrCl_3$ and 1,2,3,4,5-pentachlorocyclopentane (**4**) are the only reaction products observed. After separation from the organic component, $CpZrCl_3$ is obtained in an almost quantitative yield practically free from Cp_2ZrCl_2 and $ZrCl_4$.

$$\underset{\mathbf{1}}{Cp_2ZrCl_2} \xrightarrow{Cl\cdot} \underset{\mathbf{2}}{[CpZrCl_2(\eta^4\text{-}C_5H_5Cl)]} \xrightarrow{3Cl_2} \underset{\mathbf{3}}{CpZrCl_3} + \underset{\mathbf{4}}{C_5H_5Cl_5} + Cl\cdot$$

$CpZrCl_3$ thus obtained appears to be insoluble in common noncoordinating solvents. It becomes well dissolved, however, even in benzene or chloroform upon addition of donor agents ether, tetrahydrofuran, triethylamine, or pyridine in excess of 2 molar equiv. Variable-temperature ^1H NMR spectroscopy is of high diagnostic value to characterize the constitution of these adducts in solution. At room temperature in each case only one set of signals due to the added substrates is observed, indicating rapid equilibration between free and coordinated donor molecules. However, at low temperature even in the presence of an excess of the donor an adduct $CpZrCl_3(py)_2$ (py = pyridine) can be identified showing two chemically different coordinated pyridine moieties. In $CDCl_3$ solution at −45 °C we observe a sharp singlet (δ 6.65, 5 H) representing five equivalent Cp protons and two broad doublets (δ 9.0, 2 H, and δ 8.8, 2 H) resulting from orthohydrogens of coordinated pyridine ligands clearly separated from the corresponding resonance (δ 8.6, br d, 2 H) caused by free pyridine in the sample.[5] From these spectroscopic features a description of the $CpZrCl_3$ adduct with two monodentate donor ligands as (OC-6-33)-(η^5-cyclopentadienyl)bis(pyridine)zirconium(IV) trichloride[6] (**3a**) is implied. From our NMR observations it appears that such hexacoordinate zirconium(IV) complexes prefer to adopt similar structures in solution as has been disclosed by X-ray diffraction methods for the example $CpZrCl_3$(dme) (dme = 1,2-dimethoxyethane) (**3b**) in the solid state.[3a]

There is evidence, however, that the energy separation between geometrical $CpZrCl_3L_2$ isomers may not be very large in solution. In contrast to the reaction of **3** with pyridine, treatment with excess 3,5-lutidine results in the formation of three different 1:2 addition products. By its low-temperature ^1H NMR spectrum,[7] **3c**, the major component of this mixture, can be identified as being structurally equivalent to **3a** and **3b**. Both minor congeners, formed in 30% and 10% relative yield, respectively, exhibit similar NMR spectra but appear to lack the characteristic differentiation of lutidiene ligands. Above room temperature rapid equilibration of all these isomers on the NMR time scale is observed.

An etheral suspension of $CpZrCl_3$ rapidly reacts with aryllithium reagents (aryl = phenyl and *p*- and *m*-tolyl) forming tris(aryl)(η^5-cyclopentadienyl)zirconium(IV) complexes **5a–c**. Like $CpZrCl_3$, the isolated pure compounds **5b,c** are only slightly soluble in aromatic hydrocarbon solvents. They too readily form highly soluble adducts with the monodentate donor substrates mentioned above. Thus, the complex triphenylcyclopentadienylzirconium (**5a**) could only be isolated as a monoetherate. Nevertheless, rapid equilibration of free and coordinated diethyl ether can be observed with all these complexes in solution at ambient temperature by ^1H NMR spectroscopy.[8]

Experimental Section

Reactions with zirconium compounds were performed in an argon atmosphere with standard Schlenk techniques. Solvents were distilled from $P_4O_{10}(CCl_4)$ or $LiAlH_4$ prior to use. Cl_2 was dried by passing through H_2SO_4. Microanalyses were performed by Dornis und Kolbe, mikroanalytisches Laboratorium, Mülheim a. d. Ruhr.

$CpZrCl_3$. In a 500-mL two-necked Schlenk tube, equipped with a thermometer, a gas inlet tube, and a magnetic stirrer, a suspension of 30 g (0.106 mol) of Cp_2ZrCl_2 in CCl_4 (300 mL) is saturated with chlorine gas. The reaction is initiated by short irradiation (1–2 min) with a 200-W Osram sunlight lamp. Chlorine is introduced at such a rate to maintain the exothermic reaction. Occasional external cooling may be necessary to keep the temperature of the reaction mixture within the optimal range of 20–23 °C. Chlorination is complete after about 2 h. A stream of argon is passed through the resulting white suspension to remove excess chlorine. The precipitate of pure $CpZrCl_3$ is separated and washed successively with chloroform (50 mL), CCl_4 (100 mL), and pentane (100 mL). After the precipitate is dried in vacuo, $CpZrCl_3$ is obtained as a white powder; yield 26 g (96%). Anal. Calcd for $C_5H_5ZrCl_3$: C, 22.83; H, 1.92. Found: C, 22.63; H, 1.93. Evaporation of the CCl_4 filtrate yields 24 g (95%) of pentachlorocyclopentane.

$CpZrPh_3$. A 60-mL sample of a 1.1 M etheral solution of phenyllithium is added to a suspension of 4.6 g (17 mmol) of $CpZrCl_3$ in 300 mL of ether at −30 °C over a period of 30 min. The reaction mixture is allowed to warm up and is then stirred at 0 °C for 1 h. After removal of the ether in vacuo, the resulting dark residue is washed twice with cold pentane. The reaction product is dissolved in toluene (50 mL) at +5 °C and filtered cold from lithium chloride. Addition of the resulting clear solution to 300 mL of pentane at −10 °C precipitates $CpZrPh_3\cdot Et_2O$, obtained as a pale yellow solid after filtration and drying in vacuo; yield 4.6 g (58%). Anal. Calcd for $C_{27}H_{30}OZr$: C, 70.23; H, 6.55; Found: C, 70.27, H, 6.51. Tris(*p*- and *m*-tolyl)cyclopentadienylzirconium complexes have been obtained by analogous procedures. Anal. Calcd for $C_{26}H_{26}Zr$: C, 72.67; H, 6.1; Found (**5b**): C, 72.69; H, 6.6. Found (**5c**): C, 73.18; H, 6.16.

Registry No. **1**, 1291-32-3; **3**, 34767-44-7; **3a**, 80327-21-5; **3c**, 80327-20-4; **5a**·Et_2O, 80327-19-1; **5b**, 80327-18-0; **5c**, 80327-17-9.

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(5) Pyridine meta and para hydrogens are not well resolved under these conditions and appear as one broad multiplet (δ 8.1–6.8); warming the sample results in line broadening and a pairwise coalescence of ortho hydrogen resonances of the differently coordinated pyridine molecules with free ones. Only one set of sharp pyridine ^1H NMR signals is observed in the limiting high-temperature spectrum at +57 °C.

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(7) ^1H NMR for **3c** ($CDCl_3$, −47 °C): δ 6.60 (s, 5H), Cp group; 8.60 (s, 2 H), 7.55 (br s, 1 H), 2.40 (s, 3 H), 8.30 (s, 2 H), 7.25 (br. s, 1 H), 2.20 (s, 3 H), 3,5-lutidine ligands.

(8) ^1H NMR (toluene-D_8, 250 MHz): for **5a**, δ 7.62 (d, 6 H), 7.04 (t, 6 H), 6.84 (t, 3 H, phenyl), 6.02 (s, 5 H, Cp); for **5b**, δ 7.58, 6.88 (AA′BB′, 12 H), 2.07 (s, 9 H, *p*-tolyl), 6.08 (s, 5 H, Cp); for **5c**, δ 7.54 (s, 3 H), 7.52 (d, 3 H), 7.02 (t, 3 H), 6.69 (d, 3 H), 2.13 (s, 9 H, *m*-tolyl), 6.08 (s, 5 H, Cp). Resonances due to 1 molar equiv of coordinated diethyl ether are observed at δ 2.17 (q, 4 H) and 0.23 (t, 6 H) for **5a–c**.

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Reactions of Coordinated Molecules. 31. Rhena β-Keto Imine Derivatives of Several Biologically Important Molecules Containing 2-Ethylamino Groups

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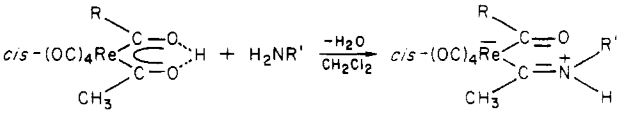
We reported recently that the rhena β-diketones **1** and **2**



1, R = CH_3
2, R = $(CH_3)_2CH$

3, R′ = H, alkyl, or aryl

condense with NH_3 and primary alkyl- or arylamines to afford