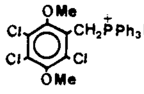

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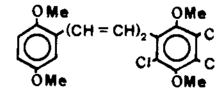

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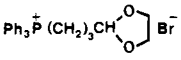

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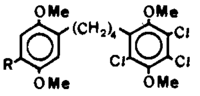
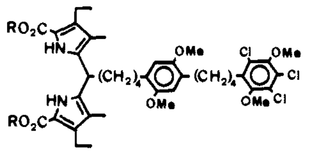
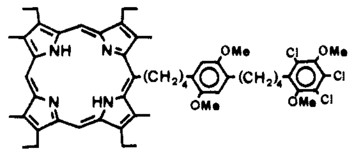


3 R = H
4 R = CHO
6 R = (CH₂)₄CHO



7 R = CH₂C₆H₅
8 R = H



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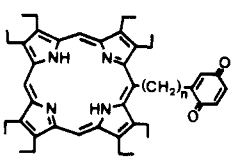

PnQ

methylenebis(pyrrole)[8] in a similar manner to Collman et al.[7] to give 9 in 24% yield. Demethylation of 9 with 30 equiv of BBr_3 at −20 °C for 2 h and then at room temperature for 5 h followed by oxidation with DDQ gave the desired compound P4Q4Q′ in 24% yield.

In ^1H NMR spectra the quinone protons of P4Q4Q′ (δ 6.42) show small upfield shift relative to 2,5-dimethyl-*p*-benzoquinone (δ 6.59). Since this shift results from the ring current of the adjacent macrocycle, the quinone rings seem to be located above the porphyrin ring. However, the electronic spectrum of P4Q4Q′ in the region of 350–650 nm is very similar to that of 5-ethyletioporphyrin (EEP),[9] indicating no significant electronic interaction among the chromophores in the ground state. A quite similar result has been obtained also in the case of P4Q.[1g] Moreover, the redox potentials (in CH_3CN vs. SCE) of the two quinones incorporated in P4Q4Q′ (−0.75, −0.22 V) are almost the same as those of the reference quinones (2,5-dimethyl-*p*-benzoquinone, −0.73 V; trichlorotoluquinone, −0.24 V). This fact also suggests negligible interaction among the three chromophores and hence the existence of the gradient redox potential in the molecule.

Detailed picosecond laser photolysis studied upon P4Q4Q′ as well as related compounds are now going on[10] and results of measurements in benzene solution are discussed briefly in this report. Picosecond transient absorption spectra were measured by means of a microcomputer-controlled double-beam picosecond spectrometer with a repetitive mode-locked Nd^{3+}/YAG laser as the excitation source.[11]

It has been confirmed that, in benzene solution, immediately after excitation (at 33-ps delay time) we can observe clearly the characteristic porphyrin cation-like band in the wavelength region of 600–800 nm in the case of both P4Q4Q′ and P4Q systems. This absorption band, which can be ascribed to the porphyrin → quinone charge-transfer state, shows approximately exponential decay in both of P4Q4Q′ and P4Q systems. However, the decay time of P4Q4Q′ (τ_{CT} ~300 ps) is much more longer than that of P4Q (τ_{CT} ~130 ps). This result demonstrates clearly the importance of the more extensive charge separation due to the multistep electron transfer for preventing the radiationless deactivation due to the back charge transfer. Of course, if the intervening methylene chain of PnQ is too long, the photoinduced charge separation becomes quite inefficient because of the very slow electron transfer. Actually, we have confirmed that it takes more than 500 ps for the photoinduced charge transfer in P6Q,[10] in contrast to the fact that we have observed clearly the porphyrin cation-like absorption band immediately after excitation in the case of P4Q4Q′.

In view of the result of P6Q, a possibility of direct electron transfer from the porphyrin to the trichloroquinone moiety owing to the coiling back of the chain seems to be small. Moreover, if such a direct electron transfer due to the coiling back occurs, the radiationless deactivation of the charge transfer state to the ground state may be easier due to the smaller energy gap than in the P4Q system, which contradicts the observed result. Therefore, the photoinduced electron transfer P4Q4Q′ seems to take place most probably by two steps along the gradient redox potential of quinone groups.

Acknowledgment. The present work was supported in part by Grants-in-Aid for Science Research (No. 56470018 and 57045075) from the Ministry of Education, Science and Culture, Japan.

Registry No. 1, 87883-35-0; **2**, 87883-36-1; 3, 87883-37-2; **4**, 87883-38-3; **5**, 76235-79-5; **6**, 87883-39-4; **7**, 87883-40-7; **8**, 87883-41-8; **9**, 87883-42-9; P4Q4Q′, 87901-19-7; EEP, 87883-43-0; benzyl 3-ethyl-4-methylpyrrole-2-carboxylate, 5866-56-8; 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-methylenebis(pyrrole), 4758-81-0; 2,5-dimethoxycinnamaldehyde, 33538-93-1.

Supplementary Material Available: Spectral data for P4Q4Q′, **2–4**, **6–9**, and EEP and electronic spectra of EEP and P4Q4Q′ (4 pages). Ordering information is given on any current masthead page.

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[8] Markovac, A.; MacDonald, S. F. *Can. J. Chem.* **1965**, *43*, 3364.

[9] EEP was prepared in a manner similar to the synthesis of **9**.

[10] Karen, A.; Okada, T.; Mataga, N., unpublished results.

[11] (a) Masuhara, H.; Ikeda, N.; Miyasaka, H.; Mataga, N. *J. Spectrosc. Soc. Jpn.* 1982, *31*, 19. (b) Martin, M. M.; Ikeda, N.; Okada, T.; Mataga, N. *J. Phys. Chem.* **1982**, *86*, 4148. (c) Miyasaka, H.; Masuhara, H.; Mataga, N. *Laser Chem.*, in press.

[12] Vedejs, E.; Arnost, M. J.; Hagen, J. P. *J. Org. Chem.* **1979**, *44*, 3230.

Stereoselectivity and Kinetic Control of Hydrogen Oxidative Addition to Iridium(I) Complexes

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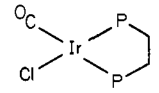
Received September 12, 1983

The oxidative addition of H_2 to d^8 square-planar complexes plays a central role in homogeneous hydrogenation and hydroformylation catalysis.[1] The reaction has been extensively studied for systems such as Vaska's complex, *trans*-$IrCl(CO)(PPh_3)_2$, and is generally thought to proceed via concerted H_2 addition leading to cis dihydride products.[2] We describe herein studies of H_2 oxidative addition with new Ir(I) complexes that indicate that subtle and previously unrecognized electronic factors are at work



1a–e, X = Cl, Br, I, CN, H; $\left.\begin{matrix}P\\P\end{matrix}\right] = Ph_2PCH_2CH_2PPh_2$ = dppe

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[1] (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (c) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 30.

[2] (a) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973, and references therein. (b) Vaska, L.; Werneke, M. F. *Ann. N. Y. Acad. Sci.* **1971**, *172*, 546–562. (c) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386–392. (d) Drouin, M.; Harrod, J. F. *Inorg. Chem.* **1983**, *22*, 999–1001. (e) Longato, B.; Morandini, F.; Bresadola, S. *Ibid.* **1976**, *15*, 650–656.

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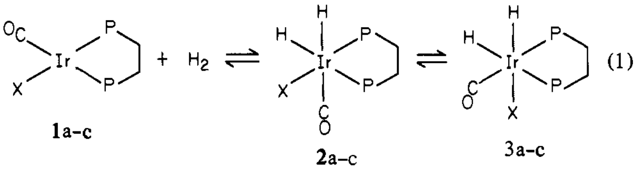
Table I. IR and NMR Data of Hydride Complexes[a]

compound	ν_{CO}, cm^{-1}	ν_{IrH}, cm^{-1}	^{1}H NMR δ_{IrH} (phosphorus couplings)	$J_{HIrH'}$	$^{31}P\{^1H\}$ NMR
2a, $IrH_2Cl(CO)(dppe)$			−7.24 (15.1, 154.5), −8.16 (18.2, 21.2)	*b*	
2b, $IrH_2Br(CO)(dppe)^c$	2000[d]	2105[d]	−7.87 (14.2, 152.2), −8.94 (~19.3[e])	*b*	36.69, 14.24[f]
2c, $IrH_2I(CO)(dppe)$			−9.05 (12.7, 147.5), −10.30 (~18.6[e])	1.2	
2d, $IrH_2(CN)(CO)(dppe)^g$	2005	2105	−9.29 (13.7, 133.6), −10.26, (~18.2[e])	*b*	31.21, 18.28[f]
2e, $IrH_3(CO)(dppe)^h$	2010	2060, 2000, 1940	−9.48 (−12.1, 124), −10.86 (19.2)	*b*	30.8 (s)[i]
3a, $IrH_2Cl(CO)(dppe)$	2045	2205, 2130	−7.89 (17.3, 134.3), −18.43 (8.8, 16.6)	5.5	
3b, $IrH_2Br(CO)(dppe)$	2040	2200, 2125	−8.34 (17.2, 132.9), −17.48 (8.6, 16.6)	5.2	35.36, 28.12[f]
3c, $IrH_2I(CO)(dppe)^j$	2035	2175	−9.17 (17.1, 130.3), −15.64 (8.6, 16.8)	4.6	
3d, $IrH_2(CN)(CO)(dppe)$			−9.71 (16.7, 123.4), −12.86 (12.1, 18.4)	4.4	31.87, 24.85[f]
4, $IrH_2(CN)(CO)(dppe)$			−9.01 (−10.5, 131.7)		

[a] IR spectra are recorded from KBr pressed pellets (Perkin-Elmer 467 spectrophotometer), ^{1}H NMR spectra are from C_6D_6 solutions (Bruker WH-400 at 400 MHz), and ^{31}P NMR spectra are from acetone-d_6 solution (Bruker WH-400 at 162 MHz, δ in ppm downfield from 85% H_3PO_4), unless otherwise indicated. Couplings are in hertz. [b] Coupling not resolved. [c] For **2b**-d_2, ν_{CO} = 2050 cm^{-1} in THF. [d] THF solution. [e] Unresolved d of d. [f] P-P coupling not resolved. Selective ^{1}H decoupling shows that the upfield resonance is coupled to a trans hydride. [g] ν_{CN} 2132 cm^{-1}. For **2d**-d_2, ν_{CO} = 2050, ν_{CN} = 2133 cm^{-1}. [h] Relative sign of J_{PH} determined by computer simulation. The coupling between the chemically equivalent hydrides is 4.5 Hz.[3a] For **2e**-d_3, ν_{CO} = 2030 cm^{-1}. [i] C_6D_6 solution. [j] For **3c**-d_2, ν_{CO} = 2037 cm^{-1}.

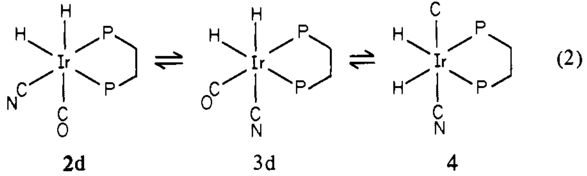
in promoting H_2 oxidative addition. The complexes employed are the mono dppe chelates **1**, which, unlike Vaska's complex, are constrained to have cis phosphine ligands.

Complexes **1a–c** (X = Cl, Br, I) are prepared by reacting $IrX_2(CO)_2^-$ with 1 equiv of dppe in THF. Initially, the five-coordinate CO adducts $IrX(CO)_2(dppe)$ are formed, but CO is readily lost yielding **1**.[3] The halide complexes **1a–c** react with H_2 in benzene at 25 °C to form sequentially two isomeric dihydride species **2** and **3**, eq 1, as determined by ^{1}H NMR spectroscopy (see Table I).[4] The stereoselective formation of **2** is complete within 1 min, and the reversibility of the reaction is shown by rapid exchange of **2** with D_2 to give **2**-d_2 and H_2 prior to formation of **3**. An equilibrium is reached between **2** and **3** over the course of several hours (K = 41, 35, and 13 at 25 °C in C_6D_6 for X = Cl, Br, and I, respectively), with the isomerization not following a simple H_2 reductive elimination–oxidative addition sequence.[5] The oxidative addition of H_2 to **1a–c** thus proceeds under kinetic control yielding initially the less stable isomer. This type of stereoselectivity is highly unusual as the kinetic and thermodynamic isomers are generally the same for H_2 oxidative addition reactions to square-planar d^8 complexes.[6]



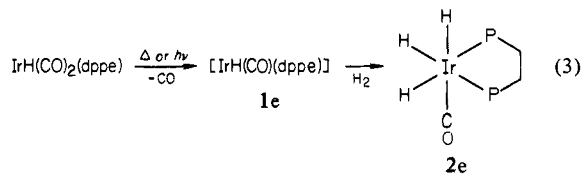
(1)

The same stereoselectivity for H_2 oxidative addition is also observed for **1d** and **1e** (X = CN and H), although in these cases the respective isomer **2** is more stable as well as kinetically preferred. The reaction of IrBr(CO)(dppe) (**1b**) with 1 equiv of PPN(CN) yields Ir(CN)(CO)(dppe) (**1d**),[7] which reversibly binds CO forming $Ir(CN)(CO)_2(dppe)$.[8] In solution Ir(CN)(CO)(dppe) and $Ir(CN)(CO)_2(dppe)$ oxidatively add H_2 rapidly, giving exclusively dihydride isomer **2d** (see Table I for IR and NMR data).[9] Isomer **2d** partially isomerizes to **3d** and **4** upon heating (eq 2). That the three isomers are in a thermal equilibrium favoring **2d** is indicated by a reversible temperature-dependent shift in the equilibrium composition.[10] Isomer **4** is noteworthy in that it cannot form by direct H_2 oxidative addition to **1d** since concerted cis addition of H_2 requires one and only one H trans to P in the dihydride product. Instead, **4** may form from **2d** or **3d** by cis reductive elimination and oxidative addition of HCN.



(2)

The monohydride complex IrH(CO)(dppe) (**1e**) has been implicated as an intermediate in the reaction of H_2 with $IrH(CO)_2(dppe)$ to form the trihydride complex **2e**, as shown in eq



(3)

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(3) (a) For **1a** and **1b** a THF solution of dppe is added to a THF solution of $[n\text{-}Bu_4N][IrX_2(CO)_2]$ at −80 °C under CO. The solution is allowed to warm to room temperature over 1 h and the product precipitated by adding ethanol and concentrating the solution. Yields are 40% for **1a** and 75% for **1b**. We have previously reported **1c**, **2e**, and $IrI(CO)_2(dppe)$: Fisher, B. J.; Eisenberg, R. *Organometallics* **1982**, *2*, 764–767. The new Ir(I) complexes are characterized as follows: **1a** IR (KBr) ν_{CO} 1983 cm^{-1}; **1b** IR (KBr) ν_{CO} 1987 cm^{-1}; $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 49.41 and 45.09 (d, J_{PP} = 13 Hz); $IrCl(CO)_2(dppe)$ IR (THF) ν_{CO} 2034, 1947 cm^{-1}; $IrBr(CO)_2(dppe)$ IR (THF) ν_{CO} 2040, 1950 cm^{-1}; $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 36.86 (s). (b) Previous reports of $IrCl(CO)_2(dppe)$ have been shown to be in error. Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971–1976.

(4) The chemical shifts and splitting patterns of the hydride resonances along with IR data allow unequivocal assignment of each structure. (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231–281. (b) Jesson, J. P. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Chapter 4. (c) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100–4101. (d) Olgemöller, B.; Beck, W. *Inorg. Chem.* **1983**, *22*, 997–998. (e) The phosphorus–hydride coupling constants for **2a–c** and **3a–c** indicate that one hydride is trans to one P and cis to the second P (J_{trans} = 120–155, J_{cis} = 12–17 Hz), while the other hydride is cis to both P donors (J_{cis} = 8–21 Hz). For **3a–c** the high-field hydride chemical shift and the high ν_{IrH} indicate a hydride trans to halide. For **2a–c** the hydride trans to CO is confirmed by a shift in ν_{CO} upon deuteration.

(5) The isomerization is markedly inhibited by added halide ion and is accelerated by contacting a benzene solution of **2** with solid $AgBF_4$. Details of the isomerization of **2** to **3** will be reported in a subsequent paper.

(6) Two reports of iridium(III) hydride complexes that appear to be kinetic but not thermodynamic products of H_2 addition are: (a) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682–684. (b) Reference 2e.

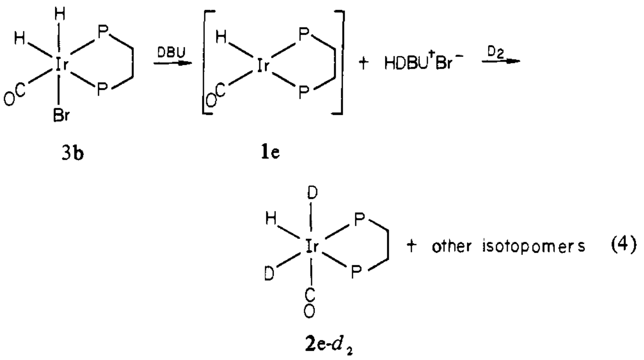
(7) IR (KBr) ν_{CO} 1997, ν_{CN} 2119 cm^{-1}; $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 51.87 and 48.91 (d, J_{PP} = 13 Hz). Compound **1d** appears to be in equilibrium with a second product (ν_{CO} 1953, ν_{CN} 2136 cm^{-1}) tentatively assigned as $IrBr(CN)(CO)(dppe)^-$ on the basis of IR and the relative increase in its IR peaks relative to **1d** upon addition of $n\text{-}Bu_4N^+Br^-$.

(8) The complex $Ir(CN)(CO)_2(dppe)$ is isolated as a pale yellow precipitate from THF–heptane solution under CO: IR (KBr) ν_{CO} 2005, 1960, ν_{CN} 2140 cm^{-1}; $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 27.4 (s).

(9) Compound **2d** is characterized spectroscopically by analogy to **2a–c** and can be precipitated from toluene–heptane solutions.

(10) Heating an acetone solution of **2d** in a sealed NMR tube at 90 °C for 25 min and then cooling quickly to 25 °C results in the composition 82% **2d**, 11% **3d**, and 7% **4**. The composition shifts to an apparent room temperature equilibrium over several days of 89% **2d**, 5% **3d**, and 6% **4**. Subsequent heating regenerates the high-temperature composition. Isomer **4** is further characterized by the structure of its hydride resonance, which is characteristic of an AA′XX′ spin system of two hydrides trans to equivalent phosphine ligands (cf. ^{1}H NMR of **2e** in ref 3a).

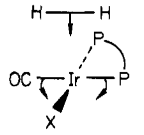
3.[3a] An alternative route to generating **1e**, which in the presence of D_2 makes possible stereochemical analysis of dihydrogen oxidative addition, involves dehydrohalogenation of compound **3b** using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. The reaction sequence is shown in eq 4 and leads to stereoselective



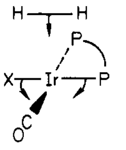
formation of **2e-d₂** with one D trans to CO.[11] A slower and subsequent scrambling reaction randomizes the deuterium label among the three hydride positions of **2e** while the total deuterium content (2D/Ir) remains constant. No evidence for the formation of the *mer* isomer **3e** is obtained at any point in the reaction sequence.

In every case we have studied, oxidative addition of H_2 to IrX(CO)(dppe) (X = Cl, Br, I, CN, H) proceeds stereoselectively, giving isomer **2** exclusively. In addition, it has been reported that the carborane complex IrX(CO)(dppe) where X = 7-C_6H_5-1,7-$B_{10}C_2H_{10}$ adds H_2 in the same way giving isomer **2**.[12] Since CO and X are both trans to a phosphine donor of dppe in IrX(CO)(dppe), the orientation of H_2 addition that leads to the observed stereoselectivity must be determined by differences between the CO and X ligands. Steric effects alone cannot account for the observed stereoselectivity since two of the ligands (X = H, CN) are sterically similar to or smaller than CO.[13] Product stability (i.e., thermodynamic control) can also be discounted as the controlling factor since only isomer **2** is formed by H_2 oxidative addition, even when isomer **3** is more stable (X = Cl, Br, I). The orientation of H_2 approach thus appears to be determined by subtle electronic effects exerted early in the course of the exothermic H_2 oxidative addition reaction.

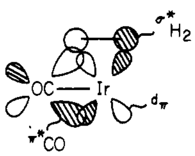
For IrX(CO)(dppe), the approach of H_2 with its molecular axis parallel to P–Ir–CO, i, is clearly preferred over a corresponding one with H_2 parallel to P–Ir–X, ii. If the key interaction in H_2



i



ii



iii

activation and oxidative addition involves donation from a filled metal d_π orbital to the H_2 antibonding σ^* orbital, as recent theoretical studies indicate,[14] then the experimental results presented here show that this $d_\pi \rightarrow \sigma^*$ interaction is facilitated in i over ii. We propose that for i, the π^* orbital of CO assists this interaction by increasing *overlap* of the filled metal-based orbital with $\sigma^*_{H_2}$, as shown in iii, thereby leading to the observed stereoselectivity as the concerted H_2 oxidative addition proceeds.

Acknowledgment. We thank the National Science Foundation (CHE80-11974 and CHE83-08064) for support of this research and the Johnson Matthey Co., Inc., for a generous loan of iridium salts. We also acknowledge helpful discussions with Professor William D. Jones.

Registry No. 1a, 87985-29-3; **1b**, 29638-05-9; **1c**, 85421-68-7; **1d**, 87985-30-6; **1e**, 87985-31-7; **2a**, 87985-32-8; **2b**, 87985-33-9; **2c**, 87985-34-0; **2d**, 87985-35-1; **2e**, 85421-67-6; **3a**, 88035-03-4; **3b**, 88035-04-5; **3c**, 88035-05-6; **3d**, 88035-06-7; **4**, 88035-07-8; Ir(CN)$(CO)_2$(dppe), 87985-36-2; [*n*-Bu_4N][$IrCl_2(CO)_2$], 73191-02-3; [*n*-Bu_4N][$IrBr_2(CO)_2$], 73190-78-0; PPN(CN), 65300-07-4.

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[11] The predominance of the isotopomer of **2e** shown in eq 4 is indicated by relative integration of the two different hydride resonances.

[12] Longato, B.; Bresadola, S. *Inorg. Chim. Acta* **1979**, *33*, 189-193.

[13] Ligand cone angles for H, CO, CN, Cl, Br, and I are 75°, ~95°, ~95°, 102°, 105°, and 107°, respectively. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-348.

[14] (a) Dedieu, A.; Strich, A. *Inorg. Chem.* **1979**, *18*, 2940-2943. (b) Sevin, A. *Nouv. J. Chim.* **1981**, *5*, 233-241. (c) Shustorovich, E. *J. Phys. Chem.* **1983**, *87*, 14-17.

Cleavage of Carbon Monoxide by Mononuclear Zirconium Dialkyls: Formation of a (μ-Oxo)dialkyl and an Enolate

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The insertion of carbon monoxide into transition-metal–alkyl bonds has been studied extensively since this elementary reaction is involved in the hydroformylation[1] and Fischer–Tropsch reaction.[2] The initial event in heterogeneous Fischer–Tropsch catalysis is thought to be dissociative chemisorption of carbon monoxide giving surface carbides and oxides, i.e., the triple bond of carbon monoxide is cleaved on the metal surface.[3] Only one example of cleavage of carbon monoxide by a mononuclear metal alkyl in homogeneous solution, in which both of the metal–oxygen and metal–carbon fragments were identified as originating from carbon monoxide, has been described.[4-6] In this communication we describe the cleavage of carbon monoxide under mild conditions by the mononuclear dialkyl $[(Me_3Si)_2N]_2ZrMe_2$.[7]

Reaction of $[(Me_3Si)_2N]_2ZrMe_2$ with carbon monoxide (1-2 atm, 20 °C, pentane) gives $\{[(Me_3Si)_2N]_2ZrMe\}_2O$ (A) and $[(Me_3Si)_2N]_2Zr(OC(Me){=}CMe_2)(Me)$ (B). The two compounds were isolated in ca. 80% yield, based upon eq 1, by fractional crystallization from pentane since A is much less soluble in that solvent than B. The (μ-oxo)dialkyl A was identified by spectroscopy[8] and X-ray crystallography (Figure 1).[9] The crystal structure of A has a crystallographically imposed center of sym-

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[6] The dihydride Cp_2ZrH_2 reacts with carbon monoxide (100 atm, 1 week) to give small amounts of $(Cp_2ZrO)_3$, derived by methylene elimination from $(Cp_2ZrCH_2O)_3$. Kroop, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353-3354.

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[8] Anal. Calcd for $C_{26}H_{78}N_4OSi_8Zr_2$: C, 35.7; H, 8.99; N, 6.45. Found: C, 35.8; H, 9.18; N, 6.16. Mp 119-121 °C(dec). The mass spectrum (chemical ionization, CH_5^+) shows an envelope of peaks centered around 868 amu, see supplementary material for the actual spectrum. NMR (PhH-d_6, 25 °C): ^{1}H δ 0.90 (s, 6 H, MeZr) and 0.42 (s, 72 H, $(Me_3Si)_2N$); ^{13}C δ 43.9 (q, $^1J_{CH}$ = 116 Hz, ZrMe) and 5.70 (q, $^1J_{CH}$ = 118 Hz, $(Me_3Si)_2N$).