Metal-Assisted Cyclization of Alkynols at a d^6 Metal Template: One-Pot Synthesis of 2-Oxacycloalkylidene Complexes of Chromium, Tungsten, and Manganese[1]

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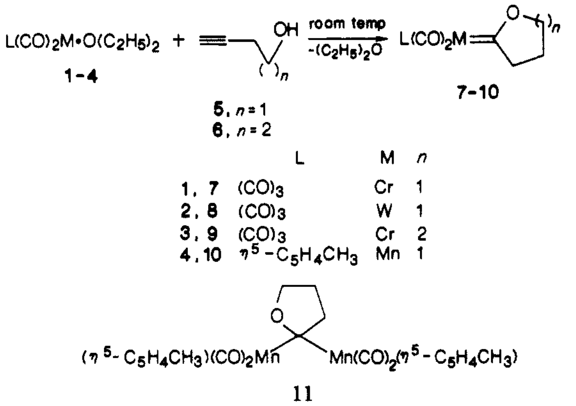
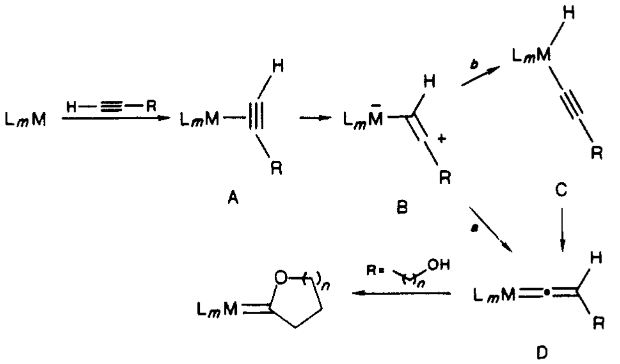
The photoinduced decarbonylation of $Cr(CO)_6$, $W(CO)_6$, and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ in ether is exploited in the metal-assisted cyclization of alkynols $HC{\equiv}C(CH_2)_nOH$ (n = 2, 3) leading to 2-oxacycloalkylidene complexes $L(CO)_2M[=\overline{CO(CH_2)_nCH_2}]$ (L $(CO)_3$, $\eta^5\text{-}C_5H_4CH_3$; M = Cr, W, Mn). The compounds are characterized both by spectroscopic means and by reaction with nucleophiles. Addition of dimethylamine results in ringopening of the carbene ligand, while 1-(diethylamino)propyne undergoes insertion into the metal-carbene bond. Reaction with methylenetrimethylphosphorane generates the conjugate base $[(CO)_5Cr\overline{CO(CH_2)_2CH}]^-$. The utility of 2-oxacycloalkylidene complexes in organic synthesis is demonstrated by functionalization of the carbene ligand into butyrolactone or 2-thiobutyrolactone upon cleavage of the metal-carbene bond by oxygen or sulfur.

Carbene ligands coordinated to a transition-metal center[2] play an important role both in stoichiometric reactions directed toward organic synthesis[3] and in catalytic processes such as olefin metathesis.[4] The most versatile route to carbene complexes is still based on the two-step addition of a nucleophile and an electrophile across the carbon-oxygen bond in metal carbonyls.[5] We report here the synthesis and reactivity of 2-oxacycloalkylidene complexes that can be prepared by cyclization of alkynols with use of a low-valent d^6 metal template. Similar compounds have been obtained from ω-haloacyl complex precursors[6-10] and via ring opening of oxiranes by metal carbene anions.[11] Another route is based on the addition of alcohol nucleophiles to vinylidene species accessible from the isomerization of terminal alkynes at a late-transition-metal center. This strategy, initiated by Chisholm and Clark,[12] has been extended to alkynols which have been reacted with a series of group VIIIb (8-10[42]) metal complexes including iron(II),[13] ruthenium(II),[14] osmium(II),[14] iridium(III),[15] nickel(II),[16] and platinum(II)[17] centers. During our studies directed toward the coupling of alkynol, carbene, and carbon monoxide ligands at chromium(0) leading to vinyl lactones,[18] we observed the cyclization of alkynols on a chromium carbonyl template generated from a vinylketene complex intermediate. We were interested in generalizing this reaction and extended our work to other metal

Scheme I



Scheme II



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templates that are readily accessible by decarbonylation of metal carbonyls.

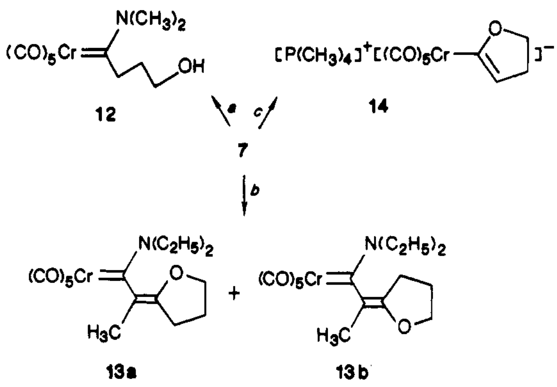
Results and Discussion

Synthesis of 2-Oxacycloalkylidene Complexes. Photolysis of ether solutions of $Cr(CO)_6$, $W(CO)_6$, or $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ at low temperature using a mercury vapor lamp and a Pyrex filter results in loss of carbon monoxide and formation of metal carbonyl solvent adducts **1**–**4**. Addition of alkynol **5** or **6** affords 2-oxacycloalkylidene complexes **7**–**10** which can be isolated as yellow to orange air-stable compounds by chromatography on silica gel (Scheme I). The formation of the cyclic carbene ligands from ω-alkynols can be rationalized in terms of a vinylidene complex intermediate D which undergoes an intramolecular nucleophilic attack of the alcohol functionality at the metal-coordinated vinylidene carbon atom (Scheme II). Experiments using a series of different metal systems have demonstrated that vinylidene complexes can be generated from terminal alkynes via 1,2-hydrogen shift.[19] These reactions are supposed to involve an intermediate η^2-alkyne complex, A, which may rearrange to its η^1-isomer B. The 1,2-hydrogen shift may occur either directly to the β-carbon atom (path a) or via oxidative addition to a σ-alkynyl–hydrido species C (path b). Whereas calculations favor a direct hydrogen transfer,[20] the oxidative addition pathway is established by experimental evidence.[21] The synthesis of the manganese complex **10** is accompanied by the formation of the red dinuclear compound **11** which may be formed by addition of a coordinatively unsaturated $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2$ fragment across the metal–carbene bond of the mononuclear species **10**.[22] The choice of the solvent is crucial for a clean reaction. For instance, the replacement of ether by a noncoordinating solvent, as has been reported recently,[23] leads generally to lower yields, in both intermolecular and intramolecular reactions. Thus, under these conditions the cyclization of alkynols cannot be competitive with the methods mentioned above.

The infrared spectra of **7**–**9** show the characteristic pentacarbonyl pattern for octahedral complexes with approximate C_{4v} symmetry. Two pairs of ν_{CO} absorptions with different intensity are observed for the mononuclear manganese complex **10**. This is due to the hindered rotation of the carbene ligand around the metal–carbene bond which is slow on the infrared time scale. Similar observations have been made for acyclic carbene ligands in $(arene)M(CO)_2$ complexes.[24] The dinuclear structure of **11** which is established by its mass spectrum involves the possibility of stereoisomers. For instance, the η^5-$C_5H_4CH_3$ ligands may be either cis or trans with respect to the manganese–manganese bond in the dimetallacyclopropane plane. Since four ν_{CO} absorptions are to be expected for both the cis and trans configuration, no assignment can be made on the basis of infrared spectroscopy. An NMR analysis of these structural features is hampered by decomposition in solution.

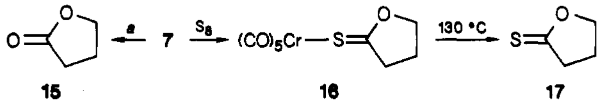
Reactivity of 2-Oxacycloalkylidene Complexes. It is a prerequisite for the use of carbene complexes in organic synthesis that the carbene ligand can be modified, functionalized, and finally cleaved from the metal by mild and high-yield methods.[25] Whereas this strategy is now widely exploited with acyclic carbene ligands,[2] only one example is known so far in which 2-oxacycloalkylidene ligands serve as synthons for organic targets.[26] The easy access to 2-oxacycloalkylidene complexes prompted us to study further functionalization of the carbene ligand effected by nucleophilic attack at the carbene atom (Scheme III).

Scheme III



^{a}$NH(CH_3)_2$. ^{b}$H_3CC{\equiv}CN(C_2H_5)_2$. ^{c}$H_2C{=}P(CH_3)_3$.

Scheme IV



^{a}$(NH_4)_2Ce(NO_3)_6$.

The isolobal analogy of alkoxycarbene complexes and esters[27] suggests for the aminolysis of 2-oxacycloalkylidene complexes a ring-opening reaction. Thus, upon treatment with dimethylamine **7** is modified into the (dimethylamino)(hydroxypropyl)carbene complex **12**. This strategy opens up an entry into new substitution patterns within the carbene ligand.

Nucleophilic multiple bond systems are known to undergo insertion into the metal–carbene bond.[28–33] This reaction has been used in the stereoselective synthesis of alkenylcarbene complexes.[34] 1-(Diethylamino)propyne reacts with **7** in toluene at room temperature to give an approximately 4/1 *E*/*Z* mixture of the (2-tetrahydrofuranyl)-2-*exo*-ethylidenylcarbene complex **13a**,**b**. The isomers can be separated by careful chromatography on silica gel.

Alkylcarbene complexes show a remarkable acidity of α-hydrogen atoms.[35] This fact has been widely exploited in the α-functionalization of carbene ligands.[11,36,37] Most conveniently the deprotonation is carried out with *n*-butyl lithium. We have tried to characterize the metal carbene anion and to isolate it as a phosphonium salt. Thus we

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reacted **7** with methylenetrimethylphosphorane in ether at low temperature. The tetramethylphosphonium salt of the conjugate metal carbene base **14** is obtained in 85% yield as a white solid which decomposes above −10 °C. Its spectroscopic data are similar to those reported for the homologous bis(triphenylphosphine)nitrogen(1+) salt.[37]

Cleavage of the Metal–Carbene Bond. An effective method to cleave the metal–carbene bond is provided by oxidation. This reaction is conveniently carried out by using cerium(IV) as an oxidizing agent. It converts **7** smoothly into γ-butyrolactone **15**. The oxidative cleavage of the carbene ligand seems to be a general reaction of chalcogens.[38] Most likely it involves a formal insertion of the group VI (6[42]) element into the metal–carbene bond.[39,40] This is confirmed by the reaction of **7** with sulfur. In boiling ether sulfur is added across the metal–carbene bond to produce the pentacarbonyl thiono lactone complex **16** in 84% isolated yield. The remarkable thermostability of this compound which must be attributed to considerable back-bonding from the metal to sulfur requires rather harsh conditions for the metal–ligand cleavage. Warming a di-*n*-butyl ether solution of **16** to 130 °C affords the free thiono lactone **17** which has been identified by comparison with an authentic sample.[41]

Experimental Section

Unless indicated otherwise all experiments were performed in an atmosphere of dried inert gas (nitrogen or argon). Solvents were dried by published techniques and distilled under inert gas before use. Infrared spectra were measured on a Perkin-Elmer 283B and on a Nicolet 5DX Fourier transform infrared spectrometer. NMR spectra were recorded on a JEOL FX 90Q or on a JEOL 270. Mass spectra were obtained on a Varian MAT 311A.

General Procedure for the Synthesis of 2-Oxacycloalkylidene Complexes 7–11. A solution of 5 mmol of metal carbonyl [$Cr(CO)_6$, $W(CO)_6$, or (η^5-$C_5H_4CH_3$)$Mn(CO)_3$] in 250 mL of ether was irradiated for 75–120 min at −30 to −50 °C by using a mercury vapor lamp (Heraeus TQ 150) and a Pyrex filter. A color change to orange (or red for the Mn complex) occurred. After addition of 7.5 mmol of alkynol (1-butynol (**5**) or 1-pentynol (**6**)) the cooling bath was removed and the mixture was stirred for 90 min. Then the solvent was removed, and the complexes **7–11** were purified by column chromatography at −25 °C using dichloromethane/pentane (1/1) [or dichloromethane/ether (1/2)] as eluent.

$(CO)_5Cr[\overline{CO(CH_2)_2C}H_2]$ (7). Recrystallization from ether/pentane (1/10) affords yellow crystals: mp 63–65 °C; yield 0.86 g (66%); IR (hexane) ν_{CO} 2065 (m), 1990 (w), 1965 (s), 1950 (vs) cm^{-1}; ^1H NMR (benzene-d_6) δ 0.50 (qui, 2 H, CH_2), 2.70 (t, 2 H, CH_2), 3.55 (t, 2 H, OCH_2); ^{13}C NMR (benzene-d_6) δ 20.3 (4-C), 60.6 (5-C), 85.3 (3-C), 217.0 (CO_{cis}), 223.8 (CO_{trans}), 341.9 ($C_{carbene}$). Anal. Calcd for $C_9H_6CrO_6$: C, 41.24; H, 2.31; Cr, 19.83; 0, 36.62; mol wt, 262.14. Found: C, 41.30; H, 2.44; Cr, 19.71; O, 36.45; mol wt, 262.

$(CO)_5W[\overline{CO(CH_2)_2C}H_2]$ (8). Recrystallization from ether/pentane (1/10) affords yellow needles: mp 64 °C; yield 1.16 g (58%); IR (hexane) ν_{CO} 2070 (m), 1987 (w), 1960 (s), 1947 (vs) cm^{-1}; ^1H NMR (benzene-d_6) δ 0.62 (qui, 2 H, CH_2), 2.52 (t, 2 H, CH_2), 3.57 (t, 2 H, OCH_2); ^{13}C NMR (benzene-d_6) 20.7 (4-C), 63.2 (5-C), 85.4 (3-C), 197.7 (CO_{cis}), 204.4 (CO_{trans}), 314.9 ($C_{carbene}$). Anal. Calcd for $C_9H_6O_6W$: C, 27.44; H, 1.53; O, 24.36; W, 46.66; mol wt, 393.99. Found: C, 27.41; H, 1.54; O, 24.38; W, 47.11; mol wt, 394 (relative to ^{184}W).

$(CO)_5Cr[\overline{CO(CH_2)_3C}H_2]$ (9). Recrystallization from ether/pentane (1/10) affords orange crystals: mp 42 °C; yield 0.40 g (29%); IR (hexane) ν_{CO} 2070 (m), 1987 (w), 1960 (s), 1947 (vs) cm^{-1}. ^1H NMR (benzene-d_6) δ 0.63 (m, 4 H, CH_2), 2.75 (m, 2 H, CH_2), 3.42 (m, 2 H, OCH_2); ^{13}C NMR (benzene-d_6) δ 15.5, 20.8 (4-, 5-C), 52.9 (6-C), 74.6 (3-C), 217.3 (CO_{cis}), 224.3 (CO_{trans}), 355.8 ($C_{carbene}$). Anal. Calcd for $C_{10}H_8CrO_6$: C, 43.50; H, 2.92; Cr, 18.83; O, 34.76; mol wt, 276.16. Found: C, 43.62; H, 2.94; Cr, 19.09; O, 34.17; mol wt, 276.

(η^5-$C_5H_4CH_3$)$(CO)_2Mn[\overline{CO(CH_2)_2C}H_2]$ (10). Chromatography on silica gel using dichloromethane/pentane as eluent affords yellow crystals: yield 0.66 g (51%); IR (hexane) ν_{CO} 1973 (s, sh), 1958 (vs), 1910 (s), 1898 (vs) cm^{-1}; ^1H NMR (benzene-d_6) δ 0.92 (qui, 2 H, CH_2), 1.77 (s, 3 H, C_5H_4–CH_3), 2.87 (t, 2 H, CH_2), 3.72 (t, 2 H, OCH_2), 4.47 (s, br, 4 H, $C_5H_4CH_3$); ^{13}C NMR (benzene-d_6) δ 13.9 (C_5H_4–CH_3), 22.3 (4-C), 56.4 (5-C), 79.7 (3-C), 86.1, 86.6, 103.3 (C_5H_4–CH_3), 233.2 (CO), 326.6 ($C_{carbene}$). Anal. Calcd for $C_{12}H_{13}MnO_3$: C, 55.40; H, 5.04; Mn, 21.11; O, 18.45; mol wt, 260.17. Found: C, 55.41; H, 5.00; Mn, 21.35; O, 18.26; mol wt, 260.

Elution of the following red band with dichloromethane/ether (1/2) affords red crystals of **μ-$[\overline{CO(CH_2)_2C}H_2][(\eta^5\text{-}C_5H_4CH_3)(CO)_2Mn]_2$ (11)**: yield 0.18 g (8%); IR (carbon disulfide) ν_{CO} 1967 (m), 1945 (vs), 1915 (vs), 1896 (w) cm^{-1}; ^1H NMR (benzene-d_6 δ 0.90 (qui, 2 H, CH_2), 1.67 (s, 3 H, $C_5H_4CH_3$), 1.77 (s, 3 H, $C_5H_4CH_3$), 2.87 (t, 2 H, CH_2), 3.73 (t, 2 H, CH_2), 4.17 (s, br, 8 H, $C_5H_4CH_3$); MS calcd for $C_{20}H_{20}Mn_2O_5$ 450.25, found 450.

$(CO)_5Cr\{C[N(CH_3)_2](CH_2)_3OH\}$ (12). A solution of 2.5 mmol of **7** in 25 mL of ether was cooled to −30 °C. Dimethylamine (7.5 mmol) was added, and the mixture was stirred for 45 min. The solvent was evaporated under high vacuum, and the yellow residue was crystallized from ether at −78 °C to give colorless crystals melting away at room temperature: yield 0.73 g (96%); IR (hexane) ν_{CO} 2055 (m), 1937 (vs), 1928 (vs, sh) cm^{-1}; ^1H NMR (benzene-d_6) δ 1.32 (m, 2 H, CH_2), 2.21 (s, 3 H, NCH_3), 2.87 (m, 2 H, CH_2), 3.05 (s, 3 H, NCH_3), 3.39 (m, 2 H, CH_2OH); ^{13}C NMR (benzene-d_6) δ 27.6 (2-C), 41.2 (NCH_3), 49.0 (1-C), 52.6 (NCH_3), 61.9 (3-C), 218.5 (CO_{cis}), 223.8 (CO_{trans}), 273.6 ($C_{carbene}$). Anal. Calcd for $C_{11}H_{13}CrNO_6$: C, 43.00; H, 4.26; Cr, 16.92; N, 4.56; O, 31.25; mol wt, 307.22. Found: C, 43.30; H, 4.28; Cr, 16.64; N, 4.45; O, 31.21; mol wt, 307.

(*E*,*Z*)-$(CO)_5Cr\{C[N(C_2H_5)_2]C(CH_3){=}\overline{CO(CH_2)_2C}H_2\}$ (13). 1-(Diethylamino)propyne (1.5 mmol) was added to a solution of 1.14 mmol of **7** in 15 mL of toluene. After the solution was stirred for 2.5 h at room temperature, the solvent was removed and the residue was purified by chromatography on silica gel using dichloromethane/ether as eluent. The first yellow band contained the *Z*-isomer **13a**: yield 0.06 g (14%); IR (hexane) ν_{CO} 2050 (m), 1967 (w), 1940 (vs), 1925 (vs), 1911 (vs) cm^{-1}; ^1H NMR (benzene-d_6) δ 0.63 (t, 3 H, (*E*)-NCH_2CH_3), 1.00 (t, 3 H, (*Z*)-NCH_2CH_3), 1.27 (m, 2 H, 4-CH_2), 1.55 (s, 3 H, CH_3), 2.00 (m, 2 H, 5-CH_2), 2.97 (m, 2 H, (*E*)-NCH_2), 3.62 (m, 4 H, (*Z*)-NCH_2, OCH_2); MS calcd for $C_{16}H_{19}CrNO_6$ 373.32, found 373. The slower moving yellow band afforded the *E*-isomer **13b**: yield 0.25 g (56%); IR (hexane) ν_{CO} 2054 (m), 1970 (w), 1935 (vs), 1917 (vs) cm^{-1}; ^1H NMR (benzene-d_6 δ 0.50 (t, 3 H, (*E*)-NCH_2CH_3), 0.97 (t, 3 H, (*Z*)-NCH_2CH_3), 1.55 (m, 2 H, 4-CH_2), 1.87 (s, 3 H, CH_3), 2.30 (m, 2 H, 5-CH_2), 2.93 (m, 2 H, (*E*)-NCH_2), 3.67 (m, 4 H, (*Z*)-NCH_2, OCH_2); MS calcd for $C_{16}H_{19}CrNO_6$ 373.32, found 373.

$[P(CH_3)_4][(CO)_5Cr\overline{CO(CH_2)_2C}H]$ (14). Methylenetrimethylphosphorane (1.80 mmol) was added to a solution of 1.14 mmol of **7** at −78 °C. A colorless precipitate was formed immediately which was washed several times with precooled ether (−78 °C) and dried under high vacuum: yield 0.42 g (85%); IR (KBr) ν_{CO} 2040 (m), 1900 (vs), 1845 (vs) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.10 (d, 12 H, PCH_3), 3.93 (t, 2 H, OCH_2, $^3J_{H,H} = 9$ Hz), 4.42 (m, 1 H, 5-CH).

Oxidative Cleavage of the Metal–Carbene Bond. A solution of 1.14 mmol of **7** in 55 mL of acetone was treated with 2.3 mmol of $(NH_4)_2Ce(NO_3)_6$ dissolved in 17 mL of acetone. A color change

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(42) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13-18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

to brown occurred, and after 1 h the mixture was concentrated and extracted with ether. The solvent was removed, and γ-butyrolactone (**15**) was characterized by comparison with an authentic sample.

$(CO)_5Cr[S{=}\overline{CO(CH_2)_2C}H_2]$ (16). Sulfur (0.4 g) was added to a solution of 5 mmol of **7** in 25 mL of ether. The mixture was warmed under reflux for 24 h and filtered. The solvent was evaporated, and the residue was purified by chromatography on silica gel at −25 °C by using dichloromethane/pentane (1/4) as eluent. After unreacted **7** (0.11 g) the thiono lactone complex **16** was obtained as yellow crystals: mp 71 °C; yield 1.23 g (84%); IR (hexane) ν_{CO} 2067 (m), 1949 (vs), 1930 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 0.93 (qui, 2 H, 4-CH_2), 2.02 (t, 2 H, 5-CH_2, $^3J_{H,H}$ = 7 Hz), 3.65 (t, 2 H, OCH_2); ^{13}C NMR (acetone-d_6) 25.2 (4-C), 45.0 (5-C), 82.5 (3-C), 216.3 (CO_{cis}), 223.8 (CO_{trans}), 228.7 ppm (1-C); Anal. Calcd for $C_9H_6CrO_6S$: C, 36.74; H, 2.05; Cr, 17.67; O, 32.63; S, 10.90; mol wt, 294.20. Found: C, 36.54; H, 2.00; Cr, 17.46; O, 32.28; S, 10.60; mol wt, 294.

$S{=}\overline{CO(CH_2)_2C}H_2$ (17). A solution of 1.4 mmol of **16** in 20 mL of di-n-butyl ether was warmed to 130 °C for 4 h. The mixture was filtered, the solvent was removed, and the residue was worked up by thick-layer chromatography. Elution with dichloromethane afforded the thiono lactone **17** which was characterized by comparison with an authentic sample; yield 0.08 g (56%).

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Registry No. **5**, 927-74-2; **6**, 5390-04-5; **7**, 54040-15-2; **8**, 58410-46-1; **9**, 98703-36-7; **10**, 108452-73-9; **11**, 1084-74-8; **12**, 108452-74-0; **13a**, 108509-38-2; **13b**, 108452-72-8; **14**, 108452-75-1; **15**, 96-48-0; **16**, 108452-76-2; **17**, 39700-44-2; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; (η^5-$C_5H_4CH_3$)$Mn(CO)_3$, 12108-13-3; H_3C-$C{\equiv}CN(C_2H_5)_2$, 4231-35-0; $H_2C{=}P(CH_3)_3$, 14580-91-7; dimethylamine, 124-40-3.

Energetics of Molybdenum–Azobenzene, Titanium–Azobenzene, Titanium–Iodide, and Titanium–Carbonyl Bonds in Bis(cyclopentadienyl) Complexes

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The energetics of Mo–N_2Ph_2, Ti–N_2Ph_2, Ti–I, and Ti–CO bonds in bis(cyclopentadienyl) complexes have been investigated. Metal–azobenzene and metal–iodine bond enthalpy terms, E(M–L), and bond dissociation enthalpies, D(M–L), were obtained by using calorimetric results for the standard enthalpies of formation of $M(Cp)_2(PhN{=}NPh)$ (M = Mo, Ti; Cp = η^5-C_5H_5) and $Ti(Cp)_2I_2$. The "low" E(M–N) values derived for the azo complexes indicate an interaction between the metal and the azobenzene ligand that is not very strong, in agreement with the proposed bonding model for $Ti(Cp)_2(PhN{=}NPh)$. Analysis of the Ti–I bond energetics enabled a discussion on the validity of transferring metal–halogen bond enthalpy terms. Knudsen effusion measurements on $Ti(Cp)_2(CO)_2$ allowed the re-evaluation of Ti–CO bond enthalpies.

Introduction

The available industrial processes for direct reduction of dinitrogen to ammonia (Haber process) or amines (Cyanamide process) require drastic conditions of temperature and pressure, which cause a high consumption of expensive and nonrenewable fossil fuels.[1,2] This has fostered the search for alternative methods to reduce dinitrogen under milder conditions.[1,2] Since the conversion of N_2 to NH_3 via the enzyme nitrogenase takes place in nature at 1 atm and 298 K and this process seems to be promoted by a transition-metal ion at the enzyme site, it should be possible to reproduce the enzymatic reactions in simple model systems.[1–4] Research efforts on the mechanism of nitrogenase action were paralleled by theoretical[1c] and experimental[1b,5] studies on the preparation, structure, bonding, and reactivity of nitrogen-containing complexes, enabling the development of catalytic systems to reduce dinitrogen to nitrogen hydrides or organic nitrogen compounds.[1b,2–4] This interest contrasts with the present paucity of data on the energetics of transition-metal–nitrogen bonds which are relevant for the N_2 fixation processes.[6–9] Thermochemical studies of transition-metal complexes containing M–N bonds have been restricted to the η^1-coordination mode,[6–9] and only in one case[9] was the ligand dinitrogen; no information exists about the energetics of η^2 coordination of azo compounds to metals despite the fact that a side-on-coordinated diimide (HN=NH) intermediate has been postulated for the activation of coordinated dinitrogen.[4]

The well-known activity of some molybdenum and titanium compounds toward activation of dinitrogen[1–4] and the common use of azobenzene as a model for diimide[10]

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