In conclusion, with the 2DECSA experiment slow spin exchange or molecular jumps can be measured for exchange times τ in the range $t_1 < \tau \lesssim T_1$, where t_1 is the preparation time of the 2D experiment (of the order of ms), and T_1 is the spin–lattice relaxation time, which for ^{13}C can be longer than 100 s. The method is an addition to the few NMR techniques by which very slow motions can be detected in solids.[8] Naturally, spin exchange between different chemical shielding tensors can be studied in the same way.

Acknowledgment. The polyethylene sample, DOWLEX 2045, was provided by Dr. Th. Scholte (D.S.M., Geleen, The Netherlands) as Chairman of the IUPAC Working Party on the Molecular Characterization of Commercial Polymers. Prof. Dr. E. de Boer and Dr. W. S. Veeman gave valuable support.

Registry No. Polyethylene (homopolymer), 9002-88-4.

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Double β-Addition of Electrophiles to Acetylide Ligands[1]

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The majority of metal carbyne complexes have been prepared by pathways involving removal of substituents from metal-bonded carbon atoms (α-carbon atom), e.g., alkoxide abstraction from alkoxycarbene complexes[2] or α-hydrogen abstraction[3] from alkylidene ligands. Other carbyne complex syntheses are based on the addition of substituents to atoms that are separated from the metal by two bonds (β-atom), e.g., alkylation or protonation of carbonyl,[4] thiocarbonyl,[5] and isocyanide[6] ligands. One of the more recently developed routes of the latter type is β-protonation or β-alkylation of terminal[7] or bridging[8] vinylidene ligands. The vinylidene complexes employed in these investigations were synthesized by isomerization or transformation of acetylene complexes or derived from carbonyl complexes. Vinylidene complexes can also be prepared from acetylide complexes by β-electrophile addition.[9] Since acetylide complexes are available in large numbers,[10] we became interested in the possibility of a new generally applicable carbyne complex synthesis starting from acetylides.

According to a recent molecular orbital study,[11] the gross atomic charge (Mulliken population analysis) at the β-carbon atom of an acetylide ligand is not changed significantly by the addition of an electrophile to give a vinylidene ligand (eq 1). Thus, a

$$[L_nMC{\equiv}CR]^x \xrightarrow{E^+} [L_nM{=}C{=}CRE]^{x+1} \tag{1}$$

second electrophile possibly could add to the same carbon atom (eq 2) provided the additional positive charge (of the first electrophile) on the vinylidene complex does not cause a sharp decrease of the reactivity toward electrophiles. This work describes the transformation of acetylide ligands into carbynes via vinylidene intermediates by double β-addition of electrophiles to acetylide ligands.

$$[L_nM{=}C{=}CRE]^{x+1} \xrightarrow{E^+} [L_nM{\equiv}CCRE_2]^{x+2} \tag{2}$$

Alkylation of the tetraethylammonium salt of the anionic pentacarbonyltungsten *tert*-butylacetylide complex[12] **1a** with FSO_3Me or $[Et_3O][BF_4]$ in CH_2Cl_2 (−70 to 20 °C) gives the deep green vinylidene complexes $(CO)_5W{=}C{=}C(CMe_3)R'$ (**2a**, R' = CH_3; **2b**, R' = C_2H_5) (eq 3). After chromatography on silica/hexane at 10 °C (or below), compounds **2** are isolated in 40–60% yield as moderately stable oils; they have been characterized by mass spectrometry and by spectroscopic means.[13] Complexes **2** are the first isolable pentacarbonyl tungsten vinylidene complexes.[14]

$$\underset{\mathbf{1a}}{[NEt_4][(CO)_5WC{\equiv}CCMe_3]} \xrightarrow[CH_2Cl_2,\ -70\ \text{to}\ 20\ ^\circ C]{FSO_3Me\ \text{or}\ [Et_3O][PF_6]} \underset{\substack{\mathbf{2a},\ R' = CH_3 \\ \mathbf{2b},\ R' = C_2H_5}}{(CO)_5W{=}C{=}C(CMe_3)R'} \tag{3}$$

The vinylidene complexes **2** do not undergo further alkylation, however, protonation in CH_2Cl_2 (−70 to 0 °C) with a slight excess of CF_3SO_3H in the presence of iodide ions (NMe_4I) provides the carbyne complexes *trans*-$I(CO)_4W{\equiv}CCH(CMe_3)R'$ (**3a**, R' = CH_3; **3b**, R' = C_2H_5) in almost quantitative spectroscopic yield (IR) (eq 4). After neutralization of the excess acid with Na_2CO_3, the solvent is removed, and the products are recrystallized from CH_2Cl_2/hexane (50–70% isolated yield). Due to the thermal lability of the tetracarbonylcarbyne complexes **3**, all procedures have to be performed at temperatures at or below 0 °C. The complexes are easily characterized by their spectroscopic data[15]

$$\mathbf{2} \xrightarrow[CH_2Cl_2]{CF_3SO_3H/NMe_4I} \underset{\mathbf{3}}{I(CO)_4W{\equiv}CCH(CMe_3)R'} \tag{4}$$

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(13) **2a**: MS (m/e, ^{184}W) 420; IR cm^{-1}, cyclohexane) ν_{CO} 2088 (w), 1986 (sh, w), 1977 (vs), 1969 (s), $\nu_{C=C}$ 1664 (w); ^{13}C NMR (ppm, $CDCl_3$) 376 (C_α), 211 (trans CO), 194 (cis CO), 128 (C_β). **2b**: MS (*m/e*, ^{184}W) 434; IR (cm^{-1}, cyclohexane) ν_{CO} 2088 (w), 1986 (sh,w), 1978 (vs), 1970 (sh,s), $\nu_{C=C}$ 1653 (w); ^{13}C NMR (ppm, $CDCl_3$) 382 (C_α), 210 (trans-CO), 194 (cis-CO), 134 (C_β).

(14) (a) The complex $(CO)_5W{=}C{=}CH_2$ is proposed to be formed as a reactive intermediate in the reaction of $(CO)_5W{=}C(OCH_3)CH_3$ with $LiCH_3$ and subsequent protonation: Levisalles, J.; Rudler, H.; Jeannin, Y.; Dahan, F. *J. Organomet. Chem.* **1978**, *178*, C8–C12. (b) Stable, phosphine-substituted tungsten vinylidene complexes, $(CO)_3(Ph_2PCH_2CH_2PPh_2)W{=}C{=}CHR$, have been prepared by isomerization of the corresponding acetylene complexes.[7c] (c) Homologous pentacarbonyl tungsten alleneylidene complexes, $(CO)_5W{=}C{=}C{=}CR_2$, have been synthesized: Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1982**, *115*, 695–705.

(15) ^{13}C NMR (ppm, $CDCl_2$) **3a**, 297 (C_α), 190 (CO), **3b**, 298 (C_α), 190 (CO).

as trans halide tetracarbonyltungsten carbyne complexes.[2]

Protonation of the vinylidene complexes **2** seems to be a facile process as indicated by the immediate disappearance of the deep green color during the addition of the acid at −70 °C. The first product of this protonation reaction is presumably the cationic carbyne complex $[(CO)_5W{\equiv}CCH(CMe_3)R']^+[CF_3SO_3]^-$.[16] We have studied the protonation of **2a** by ^{13}C NMR in an attempt to observe this cationic intermediate. However, the ^{13}C NMR spectrum of the reaction mixture between $(CO)_5W{=}C{=}C(CMe_3)(Me)$ (**2a**) and CF_3SO_3H (1:1, CD_2Cl_2) at −80 °C (in the absence of iodide) shows any signals that can be assigned either to the vinylidene complex **2a** or to *trans*-$CF_3SO_3(CO)_4W{\equiv}CCH(CMe_3)(Me)$ (**4**).[17] At −20 °C, only the signals of the neutral carbyne complex **4** are observed.[17] Loss of carbonyl from the cationic intermediate seems to be a fast process. Since the solubility of NMe_4I, which is used as the source of iodide ions, is very low in CH_2Cl_2, it is likely that formation of the iodo-substituted complexes **3** proceeds via *trans*-(trifluoromethanesulfonato)tetracarbonyltungsten carbyne species such as complex **4**.

Transformation of acetylide complexes into carbyne complexes is also possible in a single synthesis step. Protonation of $[NEt_4][(CO)_5WC{\equiv}CR]$, (**1a**, R = $C(CH_3)_3$; **1b**, R = C_6H_5) with excess CF_3SO_3H in the presence of NMe_4I affords the carbyne complexes *trans*-$I(CO)_4W{\equiv}CCH_2R$ (**5**) (eq 5). The reaction

$$[NEt_4][(CO)_5WC{\equiv}CR] \xrightarrow[CH_2Cl_2,\ -78\ \text{to}\ 0\ °C]{CF_3SO_3H/NMe_4I} I(CO)_4W{\equiv}CCH_2R \qquad (5)$$

1a, R = $C(CH_3)_3$
1b, R = C_6H_5
5

conditions and the workup procedure are the same as those used in the preparation of the carbyne complexes **3**. The products are isolated in 50–60% yield and easily characterized.[18]

In this protonation reaction, formation of the presumed intermediates of mono and double protonation, the neutral vinylidene complexes $(CO)_5W{=}C{=}CHR$ and the cationic complexes $[(CO)_5W{\equiv}C\text{-}CH_2R]^+$, respectively, is indicated by the appearance of a green color after addition (at −78 °C) of only 1 equiv of acid and the formation of an almost colorless solution after addition of more than 2 equiv of acid.

Double β-addition of electrophiles to acetylide ligands provides a simple access to metal carbyne complexes. Since the addition of electrophiles to β-atoms is generally more facile in electron-rich metal complexes,[4–9] this method should work particularly well for low-valent, electron-rich acetylide complexes. This work shows how it can be applied as an efficient synthesis of complexes of the type *trans*-$I(CO)_4W{\equiv}CCHRR'$ which is fundamentally different from the well-established alkoxide abstraction with BX_3 from pentacarbonyltungsten alkoxycarbene complexes.[2]

Acknowledgment. This work was supported by start-up funds of the Department of Chemistry, Princeton University, which were provided by a grant from IBM. We thank Dr. Steven A. Cohen for experimental assistance, Mary Baum for measuring the NMR spectra, and Prof. J. L. Templeton for making a manuscript of his work available to us prior to publication.

Registry No. 1a, 88780-71-6; **1b**, 88780-79-4; **2a**, 88780-72-7; **2b**, 88780-73-8; **3a**, 88780-74-9; **3b**, 88780-75-0; **4**, 88780-76-1; **5a**, 88780-77-2; **5b**, 88780-78-3.

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[16] This cationic carbyne complex may be in equilibrium with the neutral carbene complex $(CO)_5W{=}C(X)CH(CMe_3)R'$ (X = CF_3SO_3 or I). Addition of HX molecules to give carbene ligands is a common reaction for vinylidene ligands, e.g., a cationic chlorocarbene complex, $[(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeC(Cl)CH_3][BF_4]$, was synthesized by reaction of the corresponding vinylidene complex with HCl: Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 635–639.

[17] ^{13}C NMR (ppm, $CDCl_2$) **4**: 323 (C_α), 195 (CO).

[18] **5a**: MS (*m/e*, ^{184}W) 506; IR (cm^{-1}, pentane) ν_{CO} 2118 (w), 2034 (s); ^{13}C NMR (ppm, CD_2Cl_2) 291 (C_α), 190 (CO). **5b**: MS (*m/e*, ^{184}W) 526; IR (cm^{-1}, cyclohexane) ν_{CO} 2120 (w), 2038 (s); ^{13}C NMR (ppm, CD_2Cl_2) 283 (C_α), 190 (CO).

[4.4.4]Propella-2,4,7,9,12-pentaene. Synthesis and Remarkable Thermal Stability

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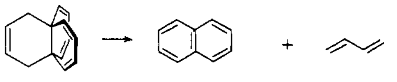
Received November 14, 1983

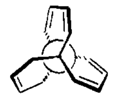
The apparent paradox that surrounds many symmetry-allowed cycloaddition reactions that pass through an aromatic transition state yet have large activation barriers has recently been analyzed.[1] The conclusion was reached that considerable energy is required to distort the reactants away from their closed-shell geometries in order to facilitate stabilizing HOMO–LUMO interaction. Trivial as it may first appear, the converse of this conclusion must also be true. For example, molecules possessing structural features highly conducive to fragmentation but held rigidly in an unsuitable conformation should prove relatively stable. Concerted bond cleavage cannot occur until the distortion is first redressed—an energy-demanding state of affairs.

A particularly relevant case in point is [4.4.4]propella-2,4,7,9,12-pentaene (**1**), the most highly unsaturated propellane known to date. Inference has earlier been made on the basis of limited experimental data that **1** is particularly prone to retrograde Diels–Alder fragmentation,[2] presumably to naphthalene and butadiene. However, Dreiding models of **1** clearly indicate the molecule to exist in one or the other enantiomerically related conformation A or B, in line with X-ray crystal data for lesser unsaturaed analogues.[3] Not only are the double bonds in its cyclohexadiene rings not mutually coplanar, but the C(1)–C(11) and C(6)–C(14) single bonds of the cyclohexene subunit are pronouncedly tilted in opposite directions. Unambiguous is the fact that substantial topological realignment must precede fragmentation. Less obvious is the magnitude of the energy impediment that these features introduce. For these reasons, we have undertaken to synthesize **1** and the related tetraene **4** and to assess their thermal stability.[4]

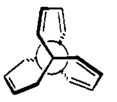


1

(1)



A



B

It must be emphasized that the structural features embodied in **1** and **4** make these molecules ideally suited to this investigation. Although both *cis*-[5] and *trans*-1,4,4a,8a-tetrahydronaphthalenes[6] are known, heating of these hydrocarbons can be expected to induce kinetically preferred electrocyclization rather than retrograde [4 + 2] fragmentation.[7] The presence of a third six-membered ring safeguards against disrotatory ring opening and introduces well-defined ground-state conformational characteristics.

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