Preparation, Properties, and Reactions of Metal-Containing Heterocycles. 73.[1] The Bis(triflate) Route to Rhenacycloalkanes

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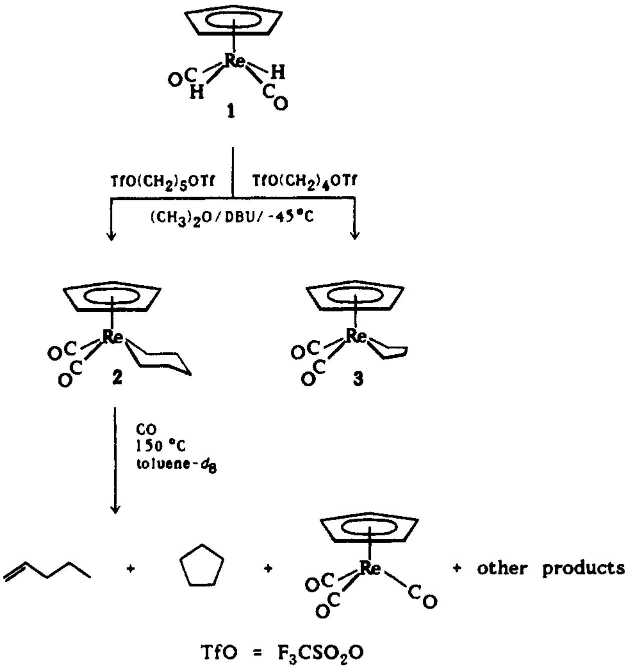
Summary: **The metallacycloalkanes $CpRe(CO)_2(CH_2)_5$ (2) and $CpRe(CO)_2(CH_2)_4$ (3) ($Cp = \eta^5\text{-}C_5H_5$) have been prepared by cationic alkylation of $CpRe(CO)_2H_2$ (1) with pentane-1,5- and butane-1,4-diylbis(trifluoromethanesulfonate), respectively, in the presence of the amine base 1,8-bicyclo[5.4.0]undec-7-ene (DBU). Both rhenium heterocyclic complexes have been identified and characterized by ^1H and $^{13}C\{^1H\}$ NMR, mass, and IR spectroscopic methods and by elemental analysis. Thermolysis of 2 results in the formation of $CpRe(CO)_3$, 1-pentene, and cyclopentane.**

Complexes containing at least two metal–carbon σ bonds are a topic of much interest in organometallic chemistry.[2a,b] Metallacycloalkanes have often been mentioned in this context, particulary concerning their role in catalytic processes.[3]

A powerful tool for the linkage of two M–C σ bonds is the bis(triflate) route, which is a variant of the cationic alkylation.[4] The excellent and inert leaving groups $CF_3SO_2O^-$ stabilize carbenium-like carbon atoms at the ends of a hydrocarbon chain,[5] thereby enabling an electrophilic attack of the terminal carbon atoms at a basic metal center. For this reason the easily available bis(triflates)[6] are superior to bis(iodides), which were only sucessful in a few cases.[7] For instance metallacycloalkanes of the iron triad with different ring size are only accessible by reaction of the corresponding bivalent metalates $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os) with alkanediylbis(trifluoromethanesulfonates).[8]

With the synthesis of the rhenacyclohexane $CpRe(CO)_2(CH_2)_5$ (2) ($Cp = \eta^5\text{-}C_5H_5$) according to the bis(triflate) method, we were able to isolate another important example of a group VII metallacycloalkane. The five-membered ring $CpRe(CO)_2(CH_2)_4$ (3) that previously has been prepared by cationic alkylation of the system $CpRe(CO)_2H_2$/DBU with diiodobutane[7b,c] was obtained by the same way.

Scheme I



Experimental Section

General Considerations. All preparations were carried out under an atmosphere of purified argon. Dimethyl ether, *n*-pentane, and THF were rendered water-free by distillation from sodium/benzophenone and degassed before use. Instrumentation: mass spectra, Varian MAT 711 A; IR, Bruker FT-IR spectrometer, Model IFS 48; ^1H, $^{13}C\{^1H\}$ NMR, Bruker AC 80 and Bruker Cryospec WM 400 at 80.13, 20.15, and 400 MHz, respectively, internal standard TMS. Elemental analyses were carried out with Carlo Erba Model 1106 and Perkin-Elmer Model 4000 atomic absorption spectrometers. The GC–MS spectra were recorded with Carlo Erba Model Fractovap 2900 chromatograph combined with a Finnigan MAT 1125 mass spectrometer. A Carlo Erba GC 6000 instrument was used to carry out GC analyses. The melting points were determined by using an Electrothermal digital melting point apparatus. The bis(triflates) $Y\text{-}(CH_2)_n\text{-}Y$ (n = 4, 5; Y = F_3CSO_2O) were prepared by treatment of tetrahydrofuran[6a] and tetrahydropyran[6b] with trifluoromethanesulfonic acid anhydride.[6a] Trifluoromethanesulfonic acid was obtained from 3M Co. (Neuss). Literature procedures were used to prepare the starting materials $Re_2(CO)_{10}$,[9] $CpRe(CO)_3$,[10] $CpRe(CO)_2Br_2$,[11] and $CpRe(CO)_2H_2$.[7c] Rhenium powder was a present from Degussa AG. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained from Merck Schuchardt and distilled prior to use.

General Preparation of the Heterocycles 2 and 3. A solution of $CpRe(CO)_2H_2$ (1) and DBU in dimethyl ether (50 mL)

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was stirred at −45 °C. A colorless precipitate appeared after several minutes. To this was added dropwise over 1 h a solution of the appropriate bis(triflate) in dimethyl ether (50 mL). The colorless mixture turned bright yellow upon stirring for 16 h. The solvent was removed under reduced pressure at −45 °C, and the residue was triturated with *n*-pentane (50 mL) and water (20 mL). After the aqueous layer was extracted with *n*-pentane (4 × 50 mL), the combined organic layers were dried with $MgSO_4$ before removal of solvent. Recrystallization of the residue from *n*-pentane (−78 °C) gave the heterocycles **2** and **3** in the form of yellow crystals.

1,1-Dicarbonyl-1-(η^5-cyclopentadienyl)rhenacyclohexane (2). **1** (240 mg, 0.71 mmol), DBU (455 mg, 2.99 mmol) and pentane-1,5-diylbis(trifluoromethanesulfonate) (262 mg, 0.71 mmol) were reacted: yield 150 mg (56%); mp 79.3 °C; IR [$\nu(C{\equiv}O)$ (*n*-pentane), cm^{-1}] 1995 (s), 1919 (s); ^1H NMR (80 MHz, $CDCl_3$, 243 K; 400 MHz, $CDCl_3$, 303 K) δ 5.27 (s, η^5-C_5H_5), 2.34–2.29 (m, 1 H), 2.19–2.15 (m, 1 H), 1.80–1.74 (m, 1 H), 1.34–1.13 (m, 5 H), 0.88–0.82 (m, 2 H) (ring methylene protons); $^{13}C\{^1H\}$ NMR (20.15 MHz, $CDCl_3$, 243 K) δ 91.3 (s, η^5-C_5H_5), 32.1 (s, γ-C), 29.3 (s, β-C), −4.8 (s, α-C); MS (FD, 50 °C) *m/e* 378/376 (M^+, $^{187}Re/^{185}Re$). Anal. Calcd for $C_{12}H_{15}O_2Re$: C, 38.18; H, 4.01; Re, 49.33. Found: C, 38.24; H, 3.94; Re, 48.27.

1,1-Dicarbonyl-1-(η^5-cyclopentadienyl)rhenacyclopentane (3). **1** (294 mg, 0.95 mmol), DBU (607 mg, 3.99 mmol) and butane-1,4-diylbis(trifluoromethanesulfonate) (337 mg, 0.95 mmol) were reacted: yield 217 mg (63%); mp 87.8 °C; IR [$\nu(C{\equiv}O)$ (*n*-pentane), cm^{-1}] 1998 (s), 1924 (s); ^1H NMR (80 MHz, $CDCl_3$, 243 K; 400 MHz, $CDCl_3$, 303 K) δ 5.32 (s, η^5-C_5H_5), 2.67–2.61 (m, 2 α-H), 2.19–2.13 (m, 2 α-H), 1.77–1.67 (m, 2 β-H), 1.60–1.52 (m, 2 β-H); $^{13}C\{^1H\}$ NMR (20.15 MHz, $CDCl_3$, 243 K) δ 90.3 (s, η^5-C_5H_5), 36.5 (s, β-C), 6.5 (s, β-C); MS (FD, 50 °C) *m/e* 364/362 (M^+, $^{187}Re/^{185}Re$). Anal. Calcd for $C_{11}H_{13}O_2Re$: C, 36.35; H, 3.60; Re, 51.23. Found: C, 36.68; H, 3.72; Re, 48.78. [Lit.[7c] ^1H NMR ($CDCl_3$) δ 5.32 (s, 5 H), 2.70 (m, 2 H), 2.20 (m, 2 H), 1.75 (m, 2 H), 1.00 (m, 2 H); IR [(*n*-pentane), cm^{-1})] 1998 (s), 1930 (vs); mp 88.5–90 °C. Found: C, 36.02; H, 3.53.]

Thermolysis of 2. (a) GC–MS experiment: a 0.5-μL aliquot of a solution of **2** (111.8 mg, 0.29 mmol) in *n*-hexane (2 mL) was injected into the GC inlet system (150 °C). Conditions: GC capillary column, SE-30 (25 m, 150 °C); carrier gas, helium (1.5 mL/min); split 1/30. MS (70 eV, 50 °C): *m/e* 378/376 (M^+, $^{187}Re/^{185}Re$), 308/306 ($M - C_5H_{10}$), 280/278 ($M - C_5H_{10} - CO$), 252/250 ($M - C_5H_{10} - 2\ CO$).

(b) A solution of **2** (250 mg, 0.66 mmol) in toluene-d_8 (1.5 mL) was heated in a pressure Schlenk tube to 150 °C for 2.5 h under an atmosphere of carbon monoxide. Subsequently, the vessel was cooled to 10 °C. The volatile products were collected under vacuum, and the obtained mixture was found to contain only 1-pentene and cyclopentane. They were identified by comparison of their ^1H NMR, GC, and GC–MS spectra to those of authentic samples. ^1H NMR (80 MHz, $CDCl_3$, 306 K): (1-pentene) δ 6.19–5.58 (m), 5.13–5.07 (m), 5.03–4.97 (m), 4.91–4.85 (m), 2.27–1.89 (m), 1.64–1.25 (m), 0.90–0.74 (m); (cyclopentane) δ 1.51 (s). GC analysis [GC inlet system: 190 °C; glass capillary column (25 m, coated with dimethyl polysiloxane, 60 °C); carrier gas, helium (1.5 mL/min); splitless]; retention time (min) 5.46 (1-pentene), 5.02 (cyclopentane). GC–MS [GC inlet system: 150 °C; GC capillary column, SE-30 (25 m, 150 °C); carrier gas, helium (1.5 mL/min); split 1/30. MS: 70 eV, 50 °C]: two GC peaks with a corresponding M^+ peak at *m/e* 70; the fragmentation patterns are those of 1-pentene and cyclopentane.[12]

The main component of the nonvolatile products was $CpRe(CO)_3$. In the ^1H NMR spectrum some additional very small unresolved proton resonances hidden in the noise of the spectra were observed. $CpRe(CO)_3$ has been isolated by chromatography (silica, CH_2Cl_2/*n*-pentane, 1:2) in 78% yield based on **2**. IR (*n*-hexane, cm^{-1}): 2031 (m), 1940 (s) [$\nu(C{\equiv}O)$ of $CpRe(CO)_3$]. ^1H NMR (80 MHz, toluene-d_8, 306 K): δ 4.41 (s, η^5-C_5H_5, $CpRe(CO)_3$).[10]

The yields of the main organic decomposition products 1-pentene and cyclopentane were determined by GC experiments to be 54% (1-pentene) and 13% (cyclopentane), respectively, based on **2**. The GC plots of exactly 2 mL of $CDCl_3$ solutions of both compounds were integrated. The measurements were compared to the results of calibrations with defined $CDCl_3$ solutions of 1-pentene and cyclopentane.

Results and Discussion

The reaction of pentane-1,5- and butane-1,4-diylbis(trifluoromethanesulfonate) with the dihydride **1** in dimethyl ether in the presence of the amine base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) leads to the rhenacycloalkanes **2** and **3** in about 60% isolated yield. Shortly after addition of the bis(triflates) to the dihydride/DBU solution, a colorless precipitate appears. Infrared spectra (*n*-pentane) of these mixtures show two weak absorption bands of $CpRe(CO)_3$ (2032, 1941 cm^{-1}) beside very strong bands of **2** (1995, 1919 cm^{-1}) and **3** (1998, 1924 cm^{-1}). These metallacyclic products were obtained by recrystallization from *n*-pentane as pale yellow, slightly air-sensitive crystals. Both rhenacycloalkanes have been identified and characterized by ^1H and $^{13}C\{^1H\}$ NMR, IR, and mass spectroscopic methods as well as by elemental analysis.

Field desorption mass spectra of the metallacycles **2** and **3** exhibit only the molecular ions in the correct intensity ratios for the naturally occurring isotopes of rhenium.

In the 5-μm region of the IR spectra of both **2** and **3**, two absorptions for terminal CO groups appear, which are due to the antisymmetrical and symmetrical stretching vibrations. The CO bands of **2** are slightly shifted to lower wavenumbers compared to those of **3**.

Bergman et al.[7c] have attributed two further peaks at 2035 and 1945 cm^{-1} to compound **3**. In our experience, however, they are caused by the CO groups of $CpRe(CO)_3$, which may be formed by decomposition of **1** or **2**. By our bis(triflate) route, the presence of this byproduct can be almost completely avoided.

The $^{13}C\{^1H\}$ NMR spectrum of **2** displays one singlet resonance at 91.3 ppm assigned to the cyclopentadienyl carbon atoms and three singlets at 32.1 ppm (γ-C atom), 29.3 ppm (β-C atoms), and −4.8 ppm (α-C atoms) assigned to the alkyl chain. The assignment for the alkyl chain carbons is made with reference to the results of labeling studies on tetracarbonylferracycloalkanes.[13] On comparison of the ^{13}C signals attributed to the α-carbon atoms of **2** and **3**, a striking difference in chemical shifts can be observed. The same results have been obtained on investigation into the corresponding tetracarbonylmetallacycloalkanes of the iron triad.[8c]

The 400-MHz ^1H NMR spectrum of **2** in $CDCl_3$ shows five alkyl resonances with multiplet structure at 2.34–2.29, 2.19–2.15, 1.80–1.74, 1.34–1.13, and 0.88–0.82 ppm in a 1:1:1:5:2 intensity ratio. The difference in their chemical shifts may be traced back to an interaction of the protons with the Cp ligand.

The values for the chemical shifts in the $^{13}C\{^1H\}$ and ^1H NMR spectra of **3** correspond to those given in the literature.[7c]

On investigations into the thermal chemistry of **2**, we found that the alkyl chain forms cyclopentane by reductive elimination and 1-pentene by β-hydrogen transfer followed by reductive elimination of the organic fragment.[8c] The main organometallic product is $CpRe(CO)_3$. Thermolysis of **2** has been carried out in the GC glass capillary column of a GC–MS apparatus and by keeping a toluene-d_8 solu-

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tion of 2 under an atmosphere of carbon monoxide at 150 °C for 2.5 h. The decomposition products have been isolated and identified by ^1H NMR, IR, GC, and GC–MS analyses.

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Stereoselective Preparation of a Rigid Trimethylenemethane Complex by Reaction of Allene with an Iridium Methylidene Derivative. X-ray Crystal Structure of *fac*-Ir[η^4-C(CH$_2$)$_3$][N(SiMe$_2$CH$_2$PPh$_2$)$_2$]

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Summary: The trimethylenemethane complex *fac*-Ir[η^4-C(CH$_2$)$_3$][N(SiMe$_2$CH$_2$PPh$_2$)$_2$] was prepared from the reaction of the methylidene derivative Ir=CH$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] with allene.

Trimethylenemethane, a structural isomer of butadiene, exists only fleetingly at ambient conditions.[1] However, this reactive organic fragment can be stabilized by coordination to a metal complex. Indeed, such complexes have been known since 1966,[2] and interest has continued culminating with the use of certain palladium allyl complexes as synthetic precursors to trimethylenemethane units in cyclopentanoid natural product synthesis.[3] Preparation of the parent trimethylenemethane ligand has for the most part used preformed C_4 fragments[4] relying on halide displacement,[5] trimethylsilyl acetate/chloride elimination,[6] ring opening of methylenecyclopropane[7] or C–H activation/elimination[8] to generate the η^4-C(CH$_2$)$_3$ unit. In this paper, we report the synthesis and X-ray crystal structure of a trimethylenemethane–iridium complex which involves carbon–carbon bond formation[9] between an iridium–methylidene derivative and allene. A surprising and unique aspect of this reaction is that the trimethylenemethane unit forms in a completely stereoselective fashion.

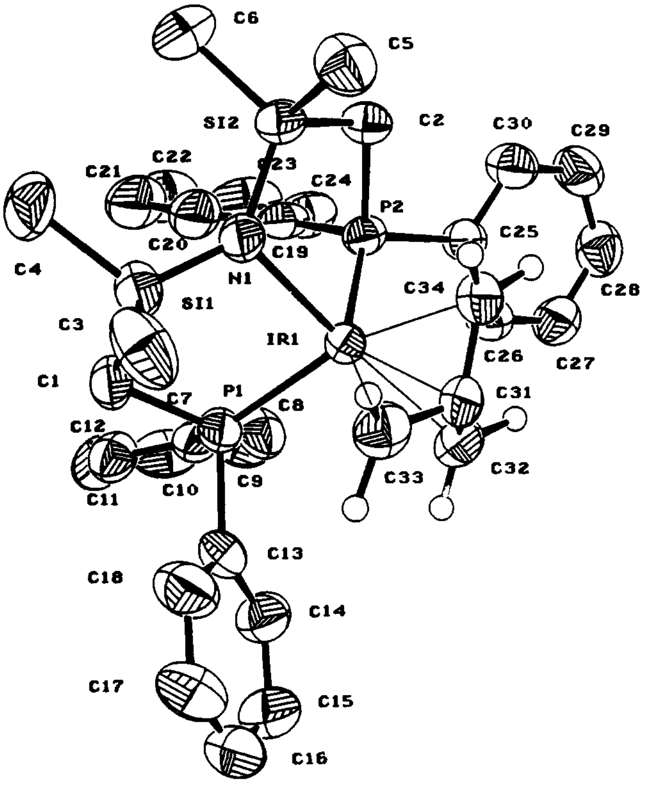

Figure 1. Molecular structure and numbering scheme for *fac*-Ir[η^4-C(CH$_2$)$_3$][N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (2). Selected bond distances (Å) and bond angles (deg) are as follows: Ir–P(1), 2.296 (1); Ir–P(2), 2.295 (1); Ir–N(1), 2.198 (4); Ir–C(31), 2.055 (5); Ir–C(32), 2.189 (5); Ir–C(33), 2.222 (5); Ir–C(34), 2.202 (5); C(31)–C(32), 1.426 (7); C(31)–C(33), 1.437 (7), C(31)–C(34), 1.441 (7); P(1)–Ir–P(2), 106.49 (5); P(1)–Ir–N(1), 87.0 (1); P(1)–Ir–C(31), 123.1 (1); P(2)–Ir–N(1), 83.0 (1); P(2)–Ir–C(31), 120.7 (1); N(1)–Ir–C(31), 126.2 (2); Ir–C(31)–C(32), 75.5 (3); Ir–C(31)–C(33), 76.8 (3); Ir–C(31)–C(34), 75.8 (3); C(32)–C(31)–C(33), 115.2 (5); C(32)–C(31)–C(34), 114.7 (5); C(33)–C(31)–C(34), 113.3 (5).

Results and Discussion

Previously, we reported[10] the structure and preparation of the iridium–methylidene complex Ir=CH$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (1). Upon exposure to allene (ca. 5

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