3396 *Organometallics* 1991, *10*, 3396-3399

Tetracarbonyl(triphenylpropenetriyl)rhenium. A Delocalized Rhenacyclobutadiene

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Received March 21, 1991

Summary: A totally delocalized tetracarbonylrhenacyclobutadiene **2** has been prepared by a ring-opening reaction of the cyclopropenylium ligand starting from $(CO)_5Re(\eta^1\text{-}C_3Ph_3)$ (**1**). The green title compound is dynamic, involving a rhenacyclobutadiene–cyclopropenyl equilibrium. Treatment of **2** with trimethylamine *N*-oxide yields a metallafuran system **4**. In reactions with diphenylacetylene or diethylacetylenedicarboxylate tricarbonyl(η^5-pentaphenylcyclopentadienyl)rhenium (**6a**) and tricarbonyl[η^5-1,2-bis(ethoxycarbonyl)-3,4,5-triphenylcyclopentadienyl]rhenium (**6b**) are formed, respectively.

Theoretical calculations[1] suggest that η^3-cyclopropenylium complexes with d^7 or d^9 ML_4 or ML_2 fragments should be susceptible to a symmetry-allowed ring-opening process. Cyclopropenylium ligands are well-known in transition-metal chemistry,[2] but the reaction leading to a four-membered metallacycle has rarely been observed in compounds with low-valent transition-metal centers. Examples are $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$ and $[Ir(CO)Cl(PMe_3)_2(C_3Ph_3)][BF_4]$.[3]

Results and Discussion

According to Scheme I we have prepared a pentacarbonyl(η^1-1,2,3-triphenylcyclopropenyl)rhenium compound **1**[4] in 70% yield starting from $NaRe(CO)_5$ and triphenylcyclopropenylium tetrafluoroborate. Upon UV irradiation **1** can be converted to the dark green tetracarbonyl(η^2-1,2,3-triphenylpropenetriyl)rhenium complex[5] **2** in 25% yield. Thermally induced loss of CO by refluxing **1** in *n*-hexane procludes **2** in varying yields together with an orange tetracarbonyl η^3-triphenyloxocyclobutenyl compound **3**.

Oxocyclobutenyl complexes[1g,6] are often observed as byproducts during the synthesis of cyclopropenyl metal complexes. The formation of **3** probably does not occur via **2**, since **3** has not been detected by treatment of **2** under 1 atm of CO. In a more likely reaction sequence **3** can be built up by a ring-expansion process via the CO insertion product (cyclopropenylcarbonyl)tetracarbonylrhenium (see also Scheme I).

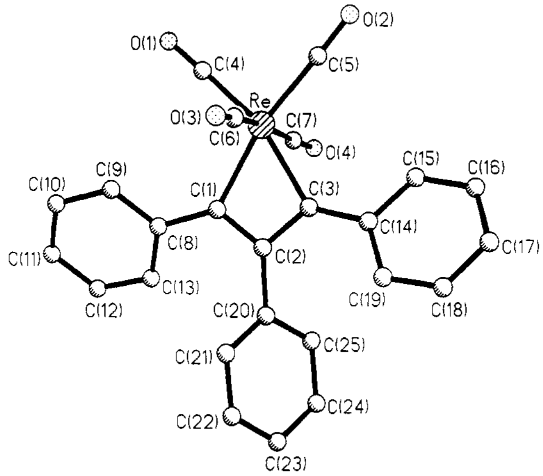

Figure 1. Crystal structure of $(CO)_4ReC_3Ph_3$ (**2a**). The hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): Re–C(1) 2.168 (7), Re–C(2) 2.741 (8), Re–C(3) 2.170 (8), C(4)–Re–C(5) 92.0 (3), C(5)–Re–C(6) 88.6 (4), C(5)–Re–C(7) 92.8 (4), C(1)–Re–C(3) 60.5 (3), Re–C(1)–C(2) 98.1 (5), C(1)–C(2)–C(3) 103.2 (7).

The X-ray structure[7] of **2a** (Figure 1) revealed that the four-membered ring is completely planar and has noncrystallographic C_{2v} symmetry. Symmetry related bond distances are equal within the limits of standard deviations. The Re–CPh bond lengths are in accord with an anticipated bond order of 1.5, expected for a delocalized metallacyclobutadiene unit.[1,8]

The low-temperature ^{13}C NMR spectrum of **2** (−50 °C) is consistent with the X-ray structure. At higher temperatures coalescence is observed for the four-membered ring system (**2a**), which is probably the result of rapid interconversion between **2a** and the η^3-cyclopropenyl complex **2b** on the NMR time scale. In a similar manner, all positionally related C_{phenyl} resonances are equilibrated as a result of the suggested dynamic process. In contrast to this observation a related asymmetrically substituted rhenacyclobutadiene complex does not show dynamic behavior.[9] The axial and equatorial CO groups of **2** do not exchange, which suggests rigidity of the $Re(CO)_4$ framework.

An equilibration process of the three-ring C atoms via a carbyne/acetylene mechanism seems to be less plausible. This is supported by the observation that treatment of **2** with di-*p*-tolylacetylene in CD_2Cl_2 at room temperature results in formation of a (η^5-1,2,3-triphenyl-4,5-di-*p*-tolylcyclopentadienyl)tricarbonylrhenium species[10] as the exclusive product. There is no indication of incorporation of *p*-tolyl groups in **2**. A similar mechanism was observed

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[7] Calculations were done on a Digital Equipment Corp. MicroVAX II using the Siemens SHELXTL-Plus software.

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[9] Padolik, L. L.; Gallucci, J.; Wojcicki, A. *J. Organomet. Chem.* **1990**, *338*, C1.

[10] (a) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046. (b) Churchill, M. R.; Ziller, J. W. *J. Organomet. Chem.* **1985**, *279*, 403. (c) A new methyl resonance is observed at 2.26 ppm in the ^1H NMR spectrum. ^{13}C NMR spectrum (CD_2Cl_2) (ppm) δ 193.88 (CO), 108.53, 108.45, 108.09 (Cp), 21.48 (Me).

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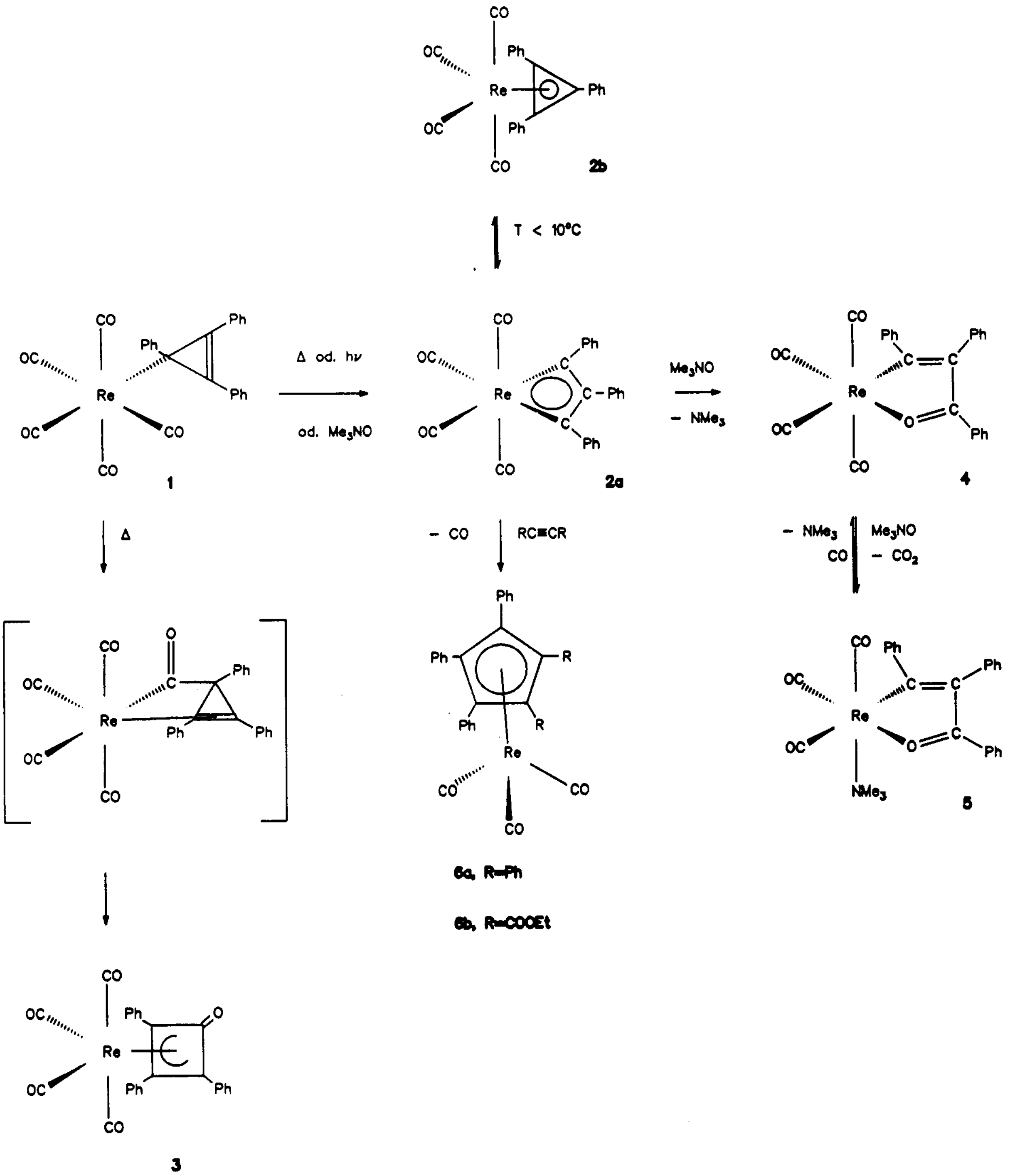
Scheme I



by Schrock and co-workers on a $(RO)_2(R'N)Re(C_3R''_3)$ system.[11]

An EHT calculation[12] on $Re(CO)_4C_3H_3$ supports the qualitative analogy of the π orbitals of 2 to those of a singlet cyclobutadiene system with four π combinations in either case.[13] The perturbation of the C_4H_4 π system by introduction of a $Re(CO)_4$ fragment causes significant energetic separation of the e-orbital set to the extent that a singlet electronic state should be preferred in $Re(CO)_4C_3Ph_3$. The HOMO (π_2) is mostly of low-lying rhenium d character and some out-of-phase p orbital admixture of the internal C_{ring} atom. The LUMO exhibits exclusively p_π character of the α-metallacyclic carbon atoms. These metal-attached centers should therefore undergo electrophilic addition reactions.

Treatment of 1 with excess trimethylamine oxide (Me_3NO) at room temperature in toluene yields 4 and 5. We believe that this occurs via formation of 2, followed by oxygen transfer of a second equivalent of Me_3NO to one of the M–C bonds of the cyclobutadiene unit to produce a tetracarbonyl-1,2,3-triphenylrhenafuran system (4).[14]

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Loss of another CO ligand induced by Me_3NO eventually leads to the red trimethylamine complex **5**. This compound can be reconverted into **4** under 1 atm CO in hot toluene. Similar complexes have in most cases been synthesized by metal-mediated coupling of an acyl group with acetylene ligands.[15]

The unusual reactivity of **2** is demonstrated not only by the ability to insert oxygen into the M-C bond but also by its cycloaddition behavior, which has already been indicated by the reaction of **2** with di-*p*-tolylacetylene. Metallacyclobutadiene complexes are known to undergo metathesis[5,11] with alkyne ligands. In contrast to these observations treatment of **2** with diphenylacetylene or diethylacetylenedicarboxylate leads exclusively to the formation of Cp derivatives[16] tricarbonyl(η^5-pentaphenylcyclopentadienyl)rhenium, $Ph_5C_5Re(CO)_3$ (**6a**), or tricarbonyl[η^5-1,2-bis(ethoxycarbonyl)-3,4,5-triphenylcyclopentadienyl]rhenium, $(EtOOC)_2Ph_3C_5Re(CO)_3$ (**6b**).

Experimental Section

All manipulations were conducted under an atmosphere of nitrogen by use of standard Schlenk techniques. Solvents for preparative purposes were dried by standard methods and distilled before use. Column chromatography was done in all cases on silica gel (Merck, Silicagel 60) at -20 °C. $Re_2(CO)_{10}$ was purchased from Johnson Matthey. $C_3Ph_3BF_4$[17] and di-*p*-tolylacetylene[18] were prepared by literature methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer at 200 and 50.3 MHz, respectively. Infrared spectra were obtained on a Bio-Rad FTS45 or Bio-Rad FTS15 spectrometer. Mass spectral analyses were performed on a Finnigan MAT 8430. Melting points were determined with use of analytically pure samples on a Büchi melting point apparatus and are uncorrected.

1. Synthesis of Pentacarbonyl(η^1-triphenylcyclopropenyl)rhenium (1). A solution of $Re_2(CO)_{10}$ (2–3 g, 3.0–4.6 mmol) in tetrahydrofuran (200 mL) was reduced by shaking over sodium amalgam for 2–2.5 h at 0 °C. The amalgam was separated off and the orange solution of $NaRe(CO)_5$ transferred to a Schlenk tube. After it was cooled to -80 °C, the mixture was treated with equimolar amounts of $C_3Ph_3BF_4$ and stirred for 2 h at that temperature. The reaction mixture was slowly warmed up to -10 °C and then pumped to dryness. The yellow residue was extracted into hexane, filtered, and crystallized at -80 °C or could be purified by column chromatography at -20 °C. Elution with toluene/hexane (1:4) produced **1** in 60–73% yield.

1: IR (hexane) ν(CO) (cm^{-1}) 2121 w, 2019 st, 2005 m, 1981 m; ^{1}H NMR (acetone-d_6) δ 8.08–6.90 mult (Ph); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 185.41 (CO), 179.67 (CO), 160.95 (C=C), 133.88, 130.79, 128.82, 128.32, 127.67, 127.46, 126.49, 123.26 (Ph), 12.76 (ReC); mp 109–111 °C (dec); EI mass spectrum, 594 $[M]^+$, 566 $[M - CO]^+$, 538 $[M - 2CO]^+$, 510 $[M - 3CO]^+$, 482 $[M - 4CO]^+$, 454 $[M - 5CO]^+$. Anal. Calcd (found) for $C_{26}H_{15}O_5Re$: C, 51.91 (52.59); H, 3.00 (2.55); Re 30.87 (31.36).

2. Preparation of Tetracarbonyl(triphenylpropenetriyl)rhenium (2). One gram (1.68 mmol) of $Re(CO)_5C_3Ph_3$ (**1**) was irradiated (mercury high-pressure lamp, 125 W) in 500 mL of hexane at -20 °C for 2 h. The volume of the green solution was reduced in vacuo to 30 mL and chromatographed over silica (Merck, Silicagel 60) at -20 °C. Elution of a green band (toluene/hexane 1:10) and recrystallization from hexane afforded **2** in 25% yield.

2: IR (hexane) ν(CO) 2075 w, 1988 st, 1981 m, 1937 w; ^{1}H NMR ($CDCl_3$, -50 °C) δ 7.52–6.73 mult (Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, -50 °C) δ 244.34 (ReC), 196.08 (CO), 193.21 (CO), 176.42 (CCC), 146.28, 139.95, 132.57, 131.93, 129.34, 128.76, 128.24, 127.60 (Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 195.78 (CO), 193.37 (CO), 131.91 br (Ph), 128.97 (Ph); mp 150–152 °C; EI mass spectra, 566 $[M]^+$, 538 $[M - CO]^+$, 510 $[M - 2CO]^+$, 482 $[M - 3CO]^+$, 454 $[M - 4CO]^+$. Anal. Calcd (found) for $C_{25}H_{15}O_4Re$: C, 53.25 (53.09); H, 2.72 (2.67); Re, 32.86 (32.92).

3. Synthesis of 2 and Tetracarbonyl(η^3-triphenyloxocyclobutenyl)rhenium (3). Refluxing 1 g (1.68 mmol) of **1** in 60 mL of hexane for ca. 3–4 h resulted in a dark green solution and an orange precipitate. The solution was decanted and worked up as described above affording **2** in 40% yield. After the orange solid was washed with hexane, pure **3** was obtained in 40% yield. Prolonged reflux (12–16 h) increases the yield of **3** up to 65% and diminishes that of **2** to 15%.

3: IR (CCl_4) ν(CO) 2036 st, 1963 m, 1935 m, ν(C=O) 1631 m; ^{1}H NMR ($CDCl_3$) δ 7.23–7.01 mult (Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 197.74 (CO), 194.99 (CO), 175.72 (C=O), 131.34, 130.89, 130.77, 130.10, 129.76, 128.67, 128.40, 127.27 (Ph), 107.22 (CCC), 78.30 (*C*C*C*); mp 203–204 °C (dec). Anal. Calcd (found) for $C_{26}H_{15}O_5Re$: C, 53.19 (52.59); H, 2.70 (2.55); Re, 31.05 (31.36).

4. Reaction between 1 and Trimethylamine *N*-Oxide. One gram (1.68 mmol) of $Re(CO)_5C_3Ph_3$ (**1**) was dissolved in toluene and treated with excess Me_3NO (1 g, 13.3 mmol; $Me_3NO{\cdot}2H_2O$ can be used instead of the water-free Me_3NO) at room temperature. The mixture first turned greenish and after 24 h resulted in a red solution. The solvent was pumped off in vacuo and the residue extracted with hexane/toluene (4:1). Column chromatography afforded **4** in traces (hexane/toluene 4:1), while elution of a red band (toluene/hexane 1:1) yielded **5** in about 70% yield after recrystallization.

4: IR (hexane) ν(CO) 2092 w, 1992 st, 1949 m; ^{1}H NMR ($CDCl_3$) δ 7.46–6.83 mult; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 241.12 (ReC), 210.84 (C=ORe), 192.42 (CO), 191.96 (CO), 187.79 (CO), 148.55 (*C*=CRe), 151.38, 138.52, 137.41, 132.65, 131.18, 130.15, 128.10, 127.97, 127.71, 126.65, 126.26, 124.64 (Ph); mp 155–157 °C; EI mass spectra, 582 $[M]^+$, 554 $[M - CO]^+$, 526 $[M - 2CO]^+$, 498 $[M - 3CO]^+$, 470 $[M - 4CO]^+$. Anal. Calcd (found) for $C_{25}H_{15}O_5Re$: C, 50.99 (51.63); H, 2.53 (2.59); Re, 31.42 (32.01).

5: IR (hexane) ν(CO) 2012 st, 1920 st, 1899 st; ^{1}H NMR (acetone-d_6) δ 7.48–6.87 mult (Ph, 15 H), 2.82 (Me, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 258.04 (ReC), 209.42 (C=ORe), 202.12 (CO), 191.49 (CO), 147.51 (ReC=*C*), 151.24, 139.35, 137.99, 132.14, 131.15, 129.94, 127.96, 127.35, 126.28, 125.90, 125.60 (Ph), 57.32 (Me); mp 152–154 °C; EI mass spectra, 613 $[M]^+$, 585 $[M - CO]^+$, 554 $[M - NMe_3]^+$, 557 $[M - 2CO]^+$, 526 $[M - NMe_3, CO]^+$, 498 $[M - NMe_3, 2CO]^+$, 442 $[M - NMe_3, 4CO]^+$. Anal. Calcd (found) for $C_{27}H_{24}NO_4Re$: C, 52.69 (52.93); H, 3.45 (3.94); N, 2.28 (2.28); Re, 30.18 (30.39).

5. Synthesis of Tetracarbonyl-1,2,3-triphenylrhenafuran (4) from Tricarbonyl(trimethylamino)-1,2,3-triphenylrhenafuran (5) and CO. $(CO)_3NMe_3ReC_3Ph_3O$ (**5**), 0.5 g (0.81 mmol), was dissolved in 60 mL of toluene. Carbon monoxide was bubbled through the red solution, which was gradually warmed up to 60 °C. After 30 min the color turned to yellow. Pumping to dryness yielded **4** quantitatively.

6. Reaction of 2 with Diphenylacetylene. **2**, 0.22 g (0.38 mmol), was treated with diphenylacetylene (tolan, 0.09 g, 0.5 mmol) under reflux in hexane (80 mL). After 1.5 h the almost colorless reaction mixture was allowed to cool to room temperature while some white precipitate formed. Reduction of the volume to 40 mL and crystallization at -80 °C resulted in 0.2 g of **6a** (72% yield) as a white powder.

6a: IR (hexane) ν(CO) 2033 st, 1937 st; ^{1}H NMR ($CDCl_3$) δ 7.34–6.93 mult; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 196.26 (CO), 128.19, 128.40, 131.34, 133.16 (Ph), 107.70 (Cp); EI mass spectra, 715 $[M]^+$, 687 $[M - CO]^+$, 659 $[M - 2CO]^+$, 631 $[M - 3CO]^+$. Anal. Calcd (found) for $C_{38}H_{25}O_3Re$: C, 64.10 (63.76); H, 3.89 (3.52); Re, 26.00 (26.01).

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Table I. Crystallographic Data for 2a

formula	$C_{25}H_{15}O_4Re$
fw	565.6
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	11.404 (2)
b, Å	12.411 (2)
c, Å	14.499 (2)
V, Å^3	2052.2 (6)
Z	4
density (calcd), g/cm^3	1.830
cryst size, mm	0.3 × 0.4 × 0.4
data collecn instrument	Siemens R3m/V
radiation	Mo Kα (λ = 0.71073 Å) graphite monochromated
linear abs coeff, cm^{-1}	60.28
temp, °C	−105
scan method	2θ–θ
2θ range, deg	2.0–57.0
F_{000}	1088
ρ factor used in weighting	0.003225
no. of unique data	5753
no. of data with $F > 8.0\sigma(F)$	4933
no. of variables	268
$R(F)$[a]	4.71
$R_w(F)$[b]	7.06
GOF	1.22

[a] $R = \sum|F_o - F_c|/\sum|F_o|$. [b] $R_w = [|w(F_o - F_c)|^2]^{1/2}/[\sum w|F_o|^2]^{1/2}$.

7. **Reaction of 2 with Diethylacetylenedicarboxylate.** 2, 0.15 g (0.26 mmol), and 0.1 mL (0.55 mmol) of diethylacetylenedicarboxylate were refluxed in hexane until the green color disappeared after 2 h. The solvent was pumped off to dryness and the resulting residue recrystallized from hexane at −30 °C yielding **6b** as pale yellow crystals (73% yield).

6b: IR (hexane) ν(CO) 2034 st, 1955 st, 1942 st, 1732 m (C=O); ^{1}H NMR (acetone-d_6) δ 7.29–7.06 mult (15 H), 4.22 q (7 Hz, 4 H), 1.18 t (7 Hz, 6 H); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 194.56 (CO), 163.75 (C=O), 133.83, 133.38, 130.74, 130.67, 129.74, 129.45, 129.05 (Ph), 111.97, 111.27, 95.99 (Cp), 62.84 (CH_2), 14.00 (CH_3).

8. **Crystallographic Study.** Single crystals were grown by cooling a hexane solution of 2 to −30 °C. A suitable crystal was sealed in a thin-walled capillary and mounted on a Siemens R3m/V diffractometer equipped with a low-temperature device. Pertinent crystallographic data are given in Table I. Cell constants and an orientation matrix for data collection were obtained from 25 centered reflections in the range 25.0° < 2θ < 30.0°. Systematic absences indicated the space group to be $P2_12_12_1$. The data were collected at −105 °C by using 2θ–θ scan techniques. Mo Kα radiation was used. The scan rate varied from 2.00 to 15.00°/min in 2θ. The Re atom was located after a Patterson search; all other non-hydrogen atoms were located from difference Fourier syntheses and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined isotropically. The final R values were calculated for $R(F)$ = 4.71 and $R_w(F)$ = 7.06.

Acknowledgment. We thank the Swiss National Foundation for support of this research.

Supplementary Material Available: Tables of crystal data and data collection parameters, atomic coordinates, and thermal parameters and complete lists of bond distances and angles for 2 (8 pages); a structure factor table for 2 (19 pages). Ordering information is given on any current masthead page.

Bonding and Conformational Aspects of Thiolato-Bridged Early–Late Heterobimetallics

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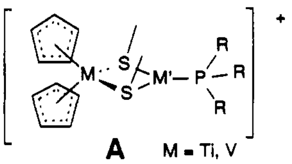
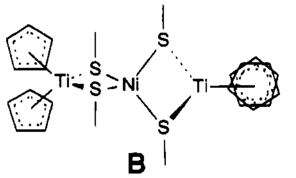
Received March 1, 1991

Summary: Extended Huckel and Fenske–Hall MO calculations have been used to examine the bonding in a series of thiolato-bridged early–late heterobimetallics. The calculations support the postulate of a weak, dative interaction between the electron-rich late metal and the electron-deficient early metal center. Generally, for Ti species the interaction is weak σ bonding in character, although for Zr there is an indication of an additional π component. When the coordination sphere of the late metal center is trigonal or square planar, these interactions result in a MS_2M' core folding and an *endo-cisoid* conformation of the substituents on the bridging S atoms is adopted. Alternatively, a endo–transoid conformation and a planar MS_2M' core is seen when the late metal center requires a pseudotetrahedral coordination geometry. The implications of these results with respect to the structural and electrochemical properties is considered.

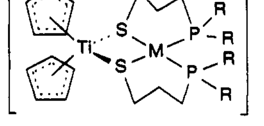
Studies of homogeneous complexes containing both an early, oxophilic and a late electron-rich metal center have been spawned by the observation of strong metal-support interactions (SMSI) in heterogeneous catalyst systems.[1] One postulate offered to explain the phenomenon of SMSI is electronic interaction between the disparate metal centers. Efforts to mimic such interactions have led to the synthesis and study of a series of homogeneous systems containing these diverse metal combinations. As part of our effort in this area, we have previously reported a variety of complexes in which thiolato ligands bridge divergent metal centers. These complexes include species of the form $[Cp_2M(\mu\text{-}SR)_2CuPR_3]^+$ (M = Ti, V) (A),[2,3] $[Cp_2Ti(\mu\text{-}SR)_2Cu(NCMe)_2]^+$ and $[Cp_2Ti(\mu\text{-}SR)_2]_2Ni$ (B),[3,4]



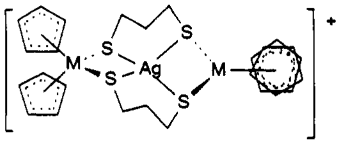
A M = Ti, V
M' = Cu, Ni



B



C M = Cu, Ni, Rh



D M = Ti, Zr,

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[1] (a) *Metal-Support Interactions in Catalysis, Sintering, and Redispersion*; Stevenson, S. A., Dumesic, J. A., Baker, R. T. K., Ruckenstein, E., Eds.; Van Nostrand Reinhold Co.: New York, 1987. (b) *Strong Metal-Support Interactions*; Baker, R. T. K., Tauster, S. J., Dumesic, J. A., Eds.; American Chemical Society; Washington, DC, 1986.

[2] Wark, T. A.; Stephan, D. W. *Inorg. Chem.* 1987, *26*, 363.

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