Final difference syntheses showed no chemically significant features, the largest being close to the metal or solvent atoms. Refinements converged smoothly to residuals given in Table VIII. Tables IX–XI report the positional parameters for the non-hydrogen atoms for these structure determinations. Full tables of interatomic distances and bond angles, displacement parameters, hydrogen atomic parameters and observed and calculated structure amplitudes are given in supplementary material (see paragraph at end of paper).

All calculations were made with programs of the SHELXTL[21] system as implemented on a Nicolet R3m/E structure-determination system. Complex neutral-atom scattering factors were taken from ref 22.

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Registry No. 1, 94282-87-8; **2**, 126083-49-6; **3**, 126083-51-0; **4**, 94282-91-4; **5**, 95402-72-5; **5**-D, 126083-58-7; **6**, 126083-55-4; **7**, 126083-52-1; **8**, 126083-53-2; **9**, 126083-54-3; **9**-D, 126083-59-8; **10**, 107040-36-8; **11**, 107080-96-6; **12**, 107040-35-7; **13**, 126083-56-5; **15**, 95402-73-6; **16**, 95402-74-7; **16**·OEt_2, 95402-75-8; **17**, 126083-57-6; $P(OMe)_3$, 121-45-9; $K[BHBu^s{}_3]$, 54575-49-4; $Li[BDEt_3]$, 74540-86-6; $P(OCD_3)_3$, 96201-07-9.

Supplementary Material Available: Tables of interatomic distances and bond angles, displacement parameters, and hydrogen atomic parameters (16 pages); a listing of observed and calculated structure factor amplitudes (68 pages). Ordering information is given on any current masthead page.

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Multiple Bonds between Transition Metals and Main-Group Elements. 73.[1a] Synthetic Routes to Rhenium(V) Alkyl and Rhenium(VII) Alkylidyne Complexes. X-ray Crystal Structures of $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_3)[CH_2C(CH_3)_3]$ and $(\eta^5\text{-}C_5Me_5)(Br)_3Re{\equiv}CC(CH_3)_3$

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Dialkyloxo(η^5-pentamethylcyclopentadienyl)rhenium(V) complexes $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_3)R'$ [$R' = C_2H_5$, $CH_2Si(CH_3)_3$, $CH_2C(CH_3)_3$], **1c–e**, have become accessible through alkylation of $(\eta^5\text{-}C_5Me_5)Re(=O)(Cl)(CH_3)$ (**7**) with R′MgCl. **1c–e** are the first rhenium complexes containing different alkyl ligands. The neopentyl derivative **1e** [$R' = CH_2C(CH_3)_3$] crystallizes in the orthorhombic space group *Pbca* with $a = 960.7$ (2), $b = 2844.5$ (4), $c = 1260.7$ (2) pm, and $Z = 8$. The X-ray crystal structure was refined to $R_w = 3.9\%$. The chiral molecule shows a distorted tetrahedral geometry around the rhenium center. The coordination of the aromatic ring ligand is highly unsymmetric due to the pronounced trans influence of the oxo ligand, with the $Re{-}C_{ring}$ bond distances varying from 217.8 (5) to 249.3 (7) pm. Different products arise from halogenation of $(\eta^5\text{-}C_5Me_5)Re(=O)(R)_2$ (**1**) with $(\eta^5\text{-}C_5H_5)TiX_3$ (**4**). Chlorination of **1f** ($R = CH_3$) with **4a** ($X = Cl$) results in formation of $(\eta^5\text{-}C_5Me_5)Re(Cl)_2(CH_3)_2$ (**9**). Chlorination of **1a** ($R = C_2H_5$) and **1h** [$R = CH(CH_3)_2$] with 2 equiv of **4a** finally yields the reduced binuclear complexes $[(\eta^5\text{-}C_5Me_5)Re(Cl)_2(\mu\text{-}Cl)]_2$ (**11**) and $[(\eta^5\text{-}C_5Me_5)Re(Cl)(\mu\text{-}Cl)]_2$ (**12**) of rhenium(IV) and rhenium(III), respectively. By way of contrast, chlorination of dialkyl complexes **1** lacking β-hydrogen atoms leads to rhenium alkylidyne complexes. Reaction of **1i** [$R = CH_2C(CH_3)_3$] with 2 equiv of **4** yields the unique *paramagnetic* rhenium(VI) complex $(\eta^5\text{-}C_5Me_5)(X)_2Re{\equiv}CC(CH_3)_3$ (**2**). Carbyne complexes **2** are quantitatively oxidized by a stoichiometric amount of the respective halogen to yield the rhenium(VII) compounds $(\eta^5\text{-}C_5Me_5)(X)_3Re{\equiv}CCMe_3$ (**3**). The tribromide **3b** has been structurally characterized. Brown crystals of **3b** belong to space group $P2_1/c$ with unit cell dimensions $a = 1311.5$ (2), $b = 723.0$ (1), $c = 1901.6$ (2) pm, $\beta = 92.68$ (1)°, and $Z = 4$. The structure refinement yielded a final R value of $R_w = 3.3\%$. The structure exhibits a "four-legged piano stool" geometry with no trans influence of the neopentylidyne ligand to the bromine atom. The rhenium–carbyne bond length is 175.5 (6) pm, typical of a rhenium–carbon triple bond. The "carbyne" angle $Re{\equiv}C{-}C$ of 179.1 (5)° corresponds to an ideal "sp geometry". Chlorination of the benzyl derivative **1g** ($R = CH_2C_6H_5$) provides the new binuclear complex $[(\eta^5\text{-}C_5Me_5)ReCl]_2(\mu\text{-}Cl)(\mu\text{-}CC_6H_5)$ (**14a**), formally a rhenium(IV) system.

Introduction

In 1975, Katz postulated that according to the Hérisson–Chauvin olefin metathesis mechanism carbyne complexes should mediate alkyne metathesis.[2a] At that time, however, hardly anything was known about such metal carbyne complexes. While for low-valent carbyne

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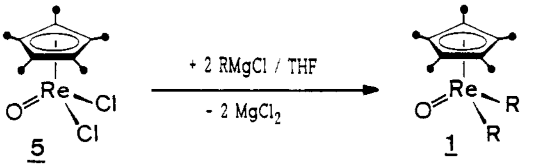
Scheme I. Alkylation of (η^5-C_5Me_5)Re(=O)$(Cl)_2$ (5) with RMgCl to 1a,b,f–i



	1a	1b	1f	1g	1h	1i
R	C_2H_5	CH_2-CH=CH_2	CH_3	$CH_2C_6H_5$	$CH(CH_3)_2$	$CH_2C(CH_3)_3$

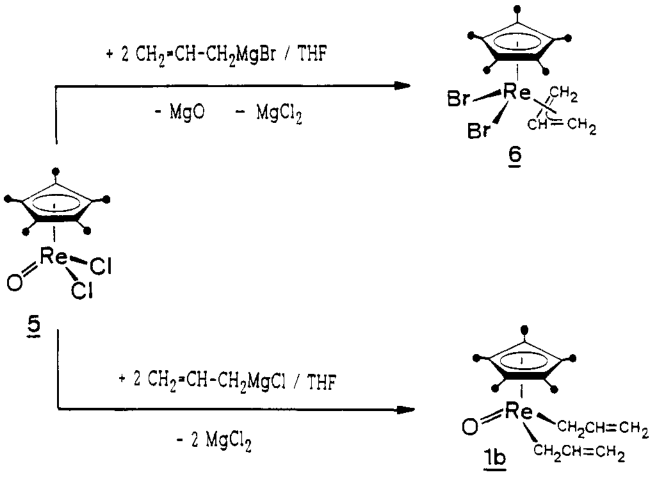
complexes that had been discovered by Fischer et al. 1 year earlier[2b,c] no example of alkyne metathesis has so far been reported, high-valent carbynes, e.g., $(RO)_3W{\equiv}CC(CH_3)_3$ [d^0 W(VI) systems], show catalytic activity in the metathesis of internal alkynes.[2c,3] In several papers Schrock proved the existence of metallacyclobutadienes as intermediates of the catalytic cycle and reports on the steric and electronic influences of the auxiliary (alkoxide) ligands. The application of MoO_3 or WO_3 on silica as heterogeneous catalysts for alkyne metathesis stresses the need of high-valent, electrophilic metal centers in such species.[4] Besides tungsten and molybdenum, rhenium is the only metal of high catalytic activity in the metathesis of olefins. Moreover, it is applied with convincing success in the metathesis of functionalized alkenes.[5] Therefore rhenium alkylidyne complexes are considered potential candidates for alkylidyne metathesis as well. Until now no d^0 Re(VII) alkylidynes containing η^5-bonded aromatic ligands were known.[6] In this paper we report on the synthesis and X-ray structure of new rhenium dialkyls of the type (η^5-C_5Me_5)Re(=O)(R)(R′) (1) as potential starting materials for the synthesis of new rhenium carbyne complexes; in addition, we describe the oxidation of the unique, paramagnetic 17e carbynes (η^5-C_5Me_5)$(X)_2Re{\equiv}CC(CH_3)_3$ (X = Cl, Br, I; 2)[7] to their diamagnetic 18e derivatives (η^5-C_5Me_5)$(X)_3Re{\equiv}CC(CH_3)_3$ (3). A single-crystal X-ray diffraction study has been carried out for the Re(VII) compound (η^5-C_5Me_5)$(Br)_3Re{\equiv}CC(CH_3)_3$ (**3b**).

Results and Discussion

I. Dialkyl(η^5-pentamethylcyclopentadienyl)oxorhenium(V) Complexes, (η^5-C_5Me_5)Re(=O)(R)(R′) (1).

Synthesis. In the context of successful chlorination of $Cp^*Re(=O)[CH_2C(CH_3)_3]_2$ (**1i**, Cp* = η^5-C_5Me_5) by means of the titanium(IV) reagent (η^5-C_5H_5)$TiCl_3$ (**4a**) to (η^5-C_5Me_5)$(Cl)_2Re{\equiv}CC(CH_3)_3$, novel dialkylrhenium(V) compounds of type **1** were synthesized and briefly communicated.[7] The dialkyl complexes **1a,b,f–i** having *identical* alkyl groups (R = R′) are formed according to Scheme I upon addition of 2.5 equiv of RMgCl to the easily available (η^5-C_5Me_5)Re(=O)$(Cl)_2$ (**5**) in THF at −78 °C.[8] After warming to ambient temperature and removing the solvent in vacuo, **1** can be extracted with *n*-pentane and purified by column chromatography on silylated silica. R can be any alkyl or aryl substituent, not being confined to ligands without β-hydrogen atoms. The resistance of **1a–c** and **1h** to β-hydride elimination could be due to the influence of the π-donor oxo ligand, which raises the energy of empty orbitals; these orbitals are then unavailable for coordination of other ligands such as the olefins that would arise from β-hydrogen elimination. A different reaction is observed by using allylmagnesium bromide as the alkylating reagent. In this special case a chlorine/bromine exchange occurs, resulting in the paramagnetic compound (η^5-C_5Me_5)$(Br)_2Re(\eta^3$-$C_3H_5)$ (**6**) of known structure.[8] This exchange reaction can be suppressed upon using allylmagnesium *chloride* instead of the *bromide* (Scheme II).

Scheme II. Alkylation of (η^5-C_5Me_5)Re(=O)$(Cl)_2$ (5) with Allylmagnesium Chloride and Bromide



1b can be isolated as a red–brown diamagnetic compound in 65% yield. The prochiral molecule **1b** has C_s symmetry. Therefore the α-protons are chemically inequivalent. The diastereotopic protons cause an ABCXY spin system in the ^1H NMR spectrum. The assignment of coupling constants was supported by a (^1H,^1H)-COSY experiment and verified by a simulated ^1H NMR spectrum. A list with all coupling constants is given in the Experimental Section. The η^1-bonding mode of the allyl ligand is further supported by the observation of two signals at 109.1 (—CH=CH_2) and 150.5 ppm (—CH=CH_2) in the olefinic region of the ^{13}C NMR spectrum and by an infrared stretching vibration band at 1615 cm^{-1} (KBr). Oxo allyl compounds are proposed intermediates in the oxidation of olefins,[9] which represents another research field of our group.[5d]

The synthesis of compounds **1c–e** that display different alkyl groups (R ≠ R′) starts with the previously reported precursor complex (η^5-C_5Me_5)Re(=O)(Cl)(CH_3) (**7**), which

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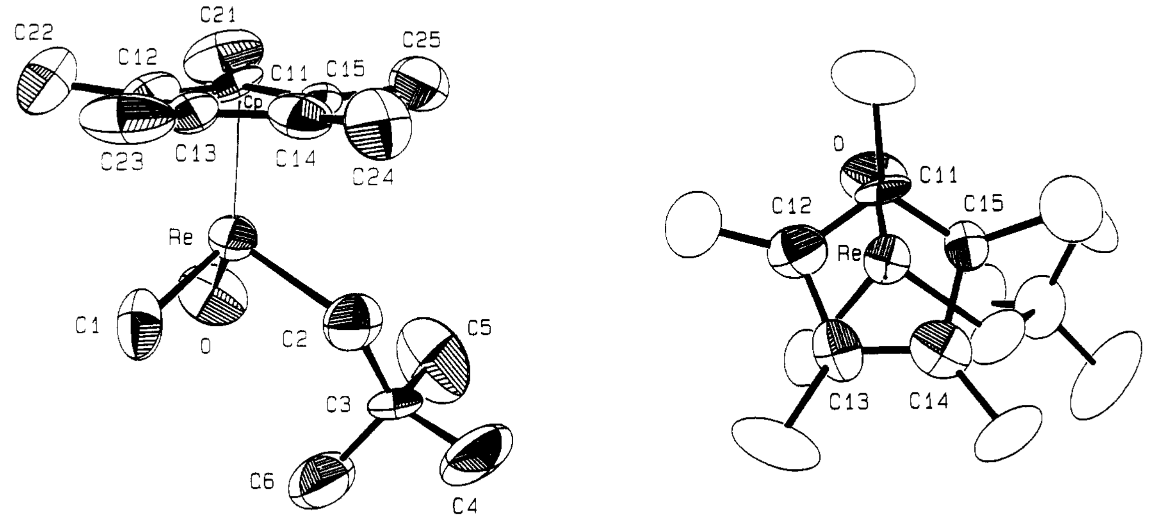

Figure 1. Two ORTEP representations of $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_3)[CH_2C(CH_3)_3]$ (**1e**): (left) side view; (right) top view. Thermal ellipsoids are at 50% probability level. Hydrogen atoms are omitted for clarity.

results quantitatively from the hydrolysis of $(\eta^5\text{-}C_5Me_5)Re(Cl)_3(CH_3)$ with a stoichiometric amount of water in the presence of pyridine.[10] The chirality of **7** (enantiomers) is demonstrated by addition of the chiral lanthanide shift reagent $Eu(hfc)_3$ [hfc = 3-(heptafluoropropylhydroxymethylene)-*d*-camphorate] to the ^1H NMR sample. The spectrum shows not only the strong shift separation of the metal-coordinated methyl group but also the doubled set of the $C_5(CH_3)_5$ signals. The ratio of the diastereometric adducts is 1/1 since no chiral influence acts at the synthesis of **7**. Attempts to separate the two enantiomers by HPLC on a chiral column (stationary phase Chirasphere, Merck) have failed so far. Alkylation of **7** with RMgCl [R = C_2H_5, $CH_2Si(CH_3)_3$, $CH_2C(CH_3)_3$] gives the chiral complexes **1c–e**. These are the first examples in organorhenium chemistry that have *different* alkyl ligands. In the meantime, other examples have been obtained in our group.[11]

Structure. A single-crystal X-ray structure of the mixed-alkyl complex $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_3)[CH_2C(CH_3)_3]$ (**1e**) revealed a distorted tetrahedral "three-legged piano stool" geometry around the metal center. The rhenium-oxygen distance of 172.7 (4) pm is typical of Re–O multiple bonds found in high-valent rhenium complexes.[12] The coordination of the five-membered π-ligand to the $Re(=O)(CH_3)[CH_2C(CH_3)_3]$ fragment is highly unsymmetric. This result is due to the pronounced trans influence of the oxo ligand. The Re–(C11⋯15) bond distances vary within the range 217.8 (5)–249.3 (7) pm (Table II). As expected, the *longer* Re–C_{ring} bonds are opposite the oxo ligand. The C–C distances within the ring deviate

Table I. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 1e[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Re	0.14019 (5)	0.15620 (<1)	0.03253 (3)	0.048
O	0.3091 (5)	0.1738 (3)	0.0572 (4)	0.079
C1	0.1066 (3)	0.1940 (2)	−0.1073 (7)	0.065
C2	0.171 (1)	0.0956 (1)	−0.0683 (8)	0.069
C3	0.3175 (2)	0.0775 (4)	−0.0948 (3)	0.063
C4	0.3011 (6)	0.0365 (2)	−0.1724 (5)	0.137
C5	0.388 (1)	0.0606 (3)	0.006 (1)	0.121
C6	0.407 (2)	0.1148 (4)	−0.1497 (9)	0.101
C11	0.0258 (6)	0.15615 (7)	0.1817 (5)	0.039
C12	−0.0357 (6)	0.19274 (8)	0.1168 (8)	0.061
C13	−0.1146 (6)	0.1657 (2)	0.0377 (3)	0.051
C14	−0.0904 (9)	0.1165 (4)	0.0476 (3)	0.059
C15	0.0035 (4)	0.1121 (4)	0.1383 (6)	0.040
C21	0.1051 (4)	0.1686 (4)	0.2849 (7)	0.090
C22	−0.047 (1)	0.2437 (2)	0.1372 (3)	0.081
C23	−0.215 (1)	0.1874 (4)	−0.0422 (6)	0.085
C24	−0.1562 (7)	0.0778 (2)	−0.0121 (3)	0.077
C25	0.040 (1)	0.06487 (8)	0.1879 (9)	0.075
Cp	−0.0422	0.1487	0.1046	

[a] The isotropic equivalent displacement parameters are defined as one-third of the trace of the orthogonalized U_{ij} tensor. Cp denotes the center of the aromatic π-ligand.

Table II. Selected Bond Distances (pm) and Angles (deg) of the Mixed-Alkyl, Chiral Organorhenium(V) Complex $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_3)[CH_2C(CH_3)_3]$ (1e)[a]

	Distances		
Re–O	172.7 (4)	Re–C15	225.3 (6)
Re–C1	209.1 (7)	Re–Cp	198.5
Re–C2	216.2 (8)	C11–C12	144.9 (9)
Re–C11	217.8 (5)	C12–C13	147.0 (9)
Re–C12	225.0 (7)	C13–C14	142.5 (9)
Re–C13	246.3 (6)	C14–C15	146.1 (9)
Re–C14	249.3 (7)	C15–C11	138.3 (9)
	Angles		
O–Re–C1	98.6 (3)	O–Re–Cp	141.2
O–Re–C2	102.1 (3)	C1–Re–Cp	107.7
C1–Re–C2	86.3 (3)	C2–Re–Cp	107.6

[a] Cp denotes the center of the pentamethylcyclopentadienyl ligand.

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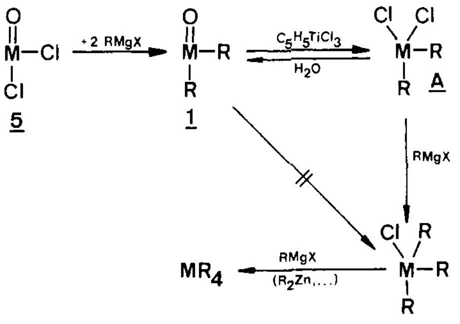
Scheme III. Successive Alkylation of (η^5-C_5Me_5)Re(=O)(Cl)$_2$ (5) To Yield Di-, Tri-, and Tetraalkylrhenium(V) Complexes[a]



[a] The synthetic route via the (isolable) intermediates A may be applied in similar sequences.

8.7 pm from each other, thus supporting the assignment of a η^3:η^2 slip of the π-ligand (allyl/olefin structure). The two enantiomers of **1e** are pairwise arranged in the unit cell around a center of symmetry.

II. Chemistry of Dialkyl(η^5-pentamethylcyclopentadienyl)oxorhenium(V) Complexes. Chlorination with (η^5-C_5H_5)$TiCl_3$ and Formation of Carbyne Complexes. After we had noticed that *direct alkylation* of (η^5-C_5Me_5)$ReCl_4$ (**8**) to the expected *dialkyl* complexes (η^5-C_5Me_5)Re(Cl)$_2$(R)$_2$ by using tetraalkyltin, dialkylzinc, and alkyl Grignard reagents is not possible due to reduction of **8** to lower valent, undefined rhenium species, we tried to substitute the oxo function of compounds **1** by two chlorine ligands. Indeed, reaction of the oxophilic reagent trichloro(η^5-cyclopentadienyl)titanium(IV) (**4a**) with (η^5-C_5Me_5)Re(=O)(CH_3)$_2$ (**1f**) gives the isolable product (η^5-C_5Me_5)Re(Cl)$_2$(CH_3)$_2$ (**9**) in 60% isolated yield (Scheme IV). Analogous to the previously reported (η^5-C_5Me_5)-Re(Cl)$_3$(CH_3) (**10**), the dimethyl derivative **9** also exhibits a strongly temperature-dependent paramagnetic shift for the metal-bonded methyl groups in the ^1H NMR spectrum.[10] While the resonance absorption appears at δ +4.69 at +20 °C, it is shifted to higher field with decreasing temperature, finally appearing at δ +2.55 at −90 °C. The temperature dependence of the paramagnetic shift of the signal can be explained by a singlet/triplet spin equilibrium. The diamagnetic singlet state predominates at room temperature and below in solution because the gradient $d\delta/dT$ increases with increasing temperature up to 30 °C.

The sequence of reactions used here can be extended and thus exploited for the *stepwise* synthesis of di-, tri-, and tetraalkyl complexes of rhenium(V) according to the general Scheme III. For example, the trimethyl complex (η^5-C_5Me_5)Re(Cl)(CH_3)$_3$[7] is not otherwise accessible, e.g., it cannot be synthesized via methylation of (η^5-C_5Me_5)-$ReCl_4$.[10b]

Quite a different type of product was obtained when **4a** was reacted with the neopentyl compound **1i** (Scheme IV). The final product was identified as the blue alkylidyne complex **2a** of composition (η^5-C_5Me_5)(Cl)$_2$Re≡CC(CH_3)$_3$.[7] The paramagnetism of **2a** [d^1 Re(VI)] was confirmed by ESR as well as by magnetic measurements in the solid state and in solution. The effective magnetic moment of **2b** was determined to be μ_{eff} = 1.58–1.61 μ_B in the temperature range from −60 to +60 °C by the Evans method[10b,13] after consideration of the relative volume change of the solvent chloroform with temperature. The theoretical value of a d^1 spin system is 1.73 μ_B. A structural assignment for the bromo compound **2b** is based on a single-crystal X-ray diffraction analysis. The overall geometry of **2b** is distorted tetrahedral. The carbon–rhenium triple bond length recorded at 167 (1) pm is extremely short, the sequence of atoms Re≡C—C is nearly linear [173 (1)°].[7]

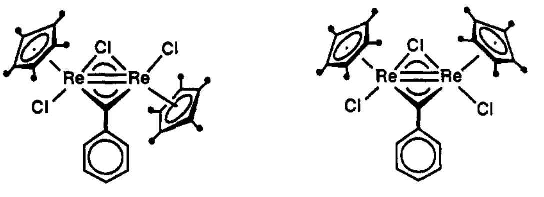


Figure 2. Two possible structures of the benzylidyne complex **14a**.

The reaction mechanism leading to the alkylidyne complexes **2** is not yet known in detail. An oxygen/chlorine exchange effected by **4a** rather likely comprises the first step; the byproduct [CpTi(=O)(Cl)]$_4$ has been identified by comparison of ^1H NMR and mass spectra with those of an authentic sample.[27] In a second step, elimination of 1 equiv of neopentane, C(CH_3)$_4$, occurs, quantified by GC/MS analysis, and an unstable rhenium(V) carbene complex could result at this stage. This latter species may subsequently be oxidized by another equivalent of the titanium reagent **4a** to give (η^5-C_5Me_5)(Cl)$_3$Re=CHC-(CH_3)$_3$, which postulated intermediate finally eliminates hydrogen chloride with concomitant formation of **2a**.[29]

To use this reaction for the synthesis of further carbyne complexes, different dialkyls **1** were applied (Scheme IV). In the case of R = C_2H_5, formation of the *ethyl* complex (η^5-C_5Me_5)Re(Cl)$_2$(C_2H_5)$_2$ has been detected by ^1H NMR spectroscopy after **1a** was treated with **4a** for 16 h at ambient temperature. If the same reaction is performed at 110 °C the reduced Re(IV) dimer [(η^5-C_5Me_5)Re(Cl)$_2$(μ-Cl)]$_2$ (**11**) is formed. A quantitative GC/MS analysis of the gas phase above the reaction solution showed that β-hydrogen shift with rapid elimination of 1 equiv of ethane occurs; the resulting, intermediate olefin complex (η^5-C_5Me_5)(Cl)$_2$Re(η^2-CH_2=CH_2) (**13a**) is probably oxidized by another equivalent of **4a** to give (η^5-C_5Me_5)(Cl)$_3$Re-(η^2-CH_2=CH_2), which then slowly eliminates 1 equiv of ethene with combination to the binuclear complex **11**. In the case of isopropyl [R = CH(CH_3)$_2$] the final product is the dinuclear complex [(η^5-C_5Me_5)Re(Cl)(μ-Cl)]$_2$ (**12**).[14] In our opinion the intermediate (η^5-C_5Me_5)(Cl)$_2$Re[η^2-CH_2=C(H)(CH_3)] (**13b**) spontaneously eliminates propene under dimerization to **12** before it is oxidized by another equivalent of (η^5-C_5H_5)$TiCl_3$. The obviously much lower stability of **13b**, which is analogous to the very stable alkyne complex series (η^5-C_5Me_5)(Cl)$_2$Re(η^2-RC≡CR),[15] as compared with **13a** is possibly due to the higher steric demand of propene versus ethylene.

We conclude that we cannot generate and isolate carbyne complexes of the type (η^5-C_5Me_5)(X)$_2$Re≡CR′ from the dialkyl precursors in case the ligands R contain β-hydrogen atoms. Therefore the dibenzyl derivative **1g** was used. After this compound was heated with 2 equiv of **4a** at 110 °C (toluene, 2 h) and the solvent removed in vacuo, the brown–violet compound **14a** was eluted with toluene from silylated silica. The ^1H NMR spectra exhibit one singlet at 1.66 ppm for the methyl groups of the π-bonded five-membered ring ligand ($CDCl_3$). The methyl/phenyl

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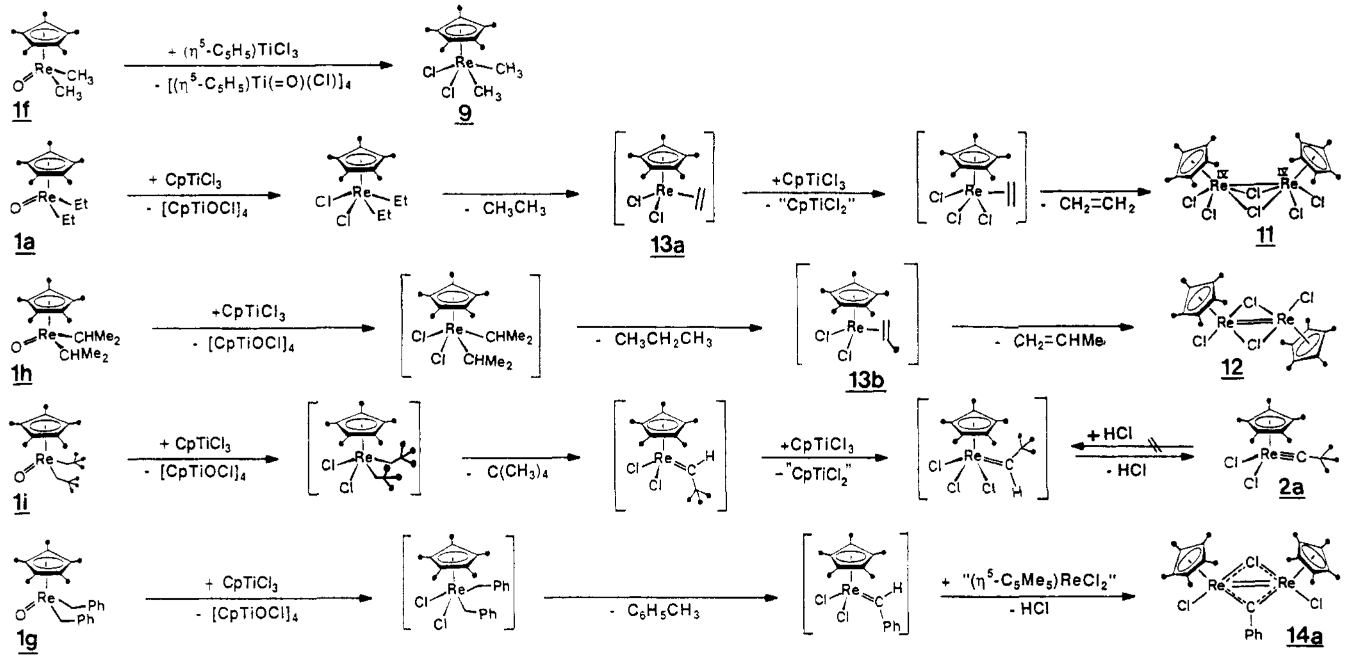
Scheme IV. Chlorination of Dialkylrhenium(V) Complexes 1 by the Organotitanium(IV) Reagent (η^5-C_5H_5)$TiCl_3$ (4a)



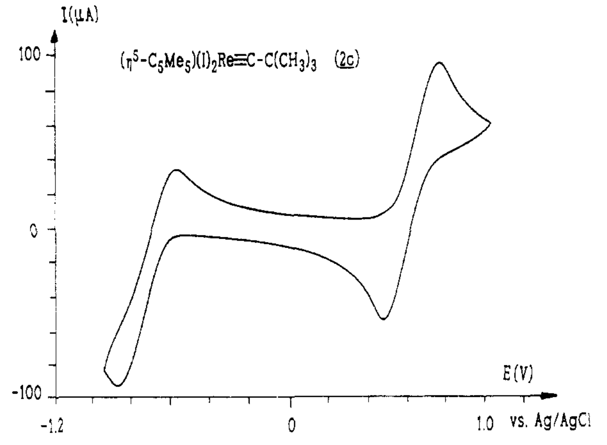


Figure 3. Cyclovoltammogram of (η^5-C_5Me_5)$(I)_2Re{\equiv}CC(CH_3)_3$ (2c).

proton ratio is 30/5 rather than 15/10 in **1g**. Important structural information arises from an EI mass spectrum. The base peak and the isotope pattern are in accordance with the formula $[(\eta^5\text{-}C_5Me_5)Re]_2(Cl)_3(CC_6H_5)$. According to the ^1H NMR spectrum there must be a symmetric structure with regard to the π-bonded ring ligands; as a matter of consequence the chlorine ligands must be arranged in a symmetrical way as well. Figure 2 shows two possible configurations of **14a**. The structures are reminiscent of the μ-carbyne complex $[(CO)_4Re]_2(\mu\text{-}CC_6H_5)(\mu\text{-}Br)$ reported by Fischer et al. in 1976.[16] In this particular 18-electron case the rhenium–rhenium distance precludes a bonding interaction (353 pm). By way of contrast, **14a** is a 16-electron complex; a rhenium-to-rhenium double bond is thus possible. A single-crystal X-ray diffraction study of **14a** is in progress.[30]

III. Redox Chemistry of (Alkylidyne)rhenium(VI) Complexes of Type (η^5-C_5Me_5)$(X)_2Re{\equiv}CC(CH_3)_3$ (2). The cyclovoltammogram of the 17-electron iodo complex **2c** shows not only a fully reversible oxidation step at 629 mV ($I_{pc}(ox)/I_{pa}(ox)$ = 0.95) but also a nearly reversible reduction step at −735 mV ($I_{pc}(red)/I_{pa}(red)$ = 1.20, Figure 3). As briefly noted in a preliminary communication,[7] oxidation of **2a** by silver hexafluoroantimonate in dichloromethane affords the diamagnetic Re(VII) complex $[(\eta^5\text{-}C_5Me_5)(Cl)_2Re{\equiv}CC(CH_3)_3]^+[SbF_6]^-$ with formation of elemental silver. Oxidation of **2b** by means of elemental bromine in tetrachloromethane at ambient temperature gives an orange-brown product of composition (η^5-C_5Me_5)$(Br)_3Re{\equiv}CC(CH_3)_3$ (**3b**). As expected, two signals of integrals 15/9 are found in the ^1H NMR spectrum for the C_5Me_5 ligand and the *tert*-butyl group. Typical of alkylidyne complexes, the carbon resonance of the sp-hybridized carbon atom shows up far downfield at δ 371.8. A field desorption mass spectrum shows the parent ion $[M]^+$ and the $[M - Br]^+$ fragment ion.

IV. Crystal and Molecular Structure of the Rhenium(VII) Alkylidyne Complex 3b. Single crystals of

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 3b[a]

atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
Re	0.24571 (2)	0.02859 (3)	0.13434 (1)	0.017
Br1	0.43535 (5)	0.12473 (9)	0.14394 (3)	0.028
Br2	0.24064 (6)	0.29712 (9)	0.04580 (3)	0.032
Br3	0.06150 (5)	0.1396 (1)	0.14952 (3)	0.029
C1	0.2575 (4)	0.0636 (8)	0.2257 (3)	0.021
C2	0.2688 (5)	0.095 (1)	0.3025 (3)	0.026
C3	0.3449 (5)	−0.045 (1)	0.3349 (4)	0.033
C4	0.3114 (6)	0.292 (1)	0.3159 (4)	0.036
C5	0.1654 (6)	0.079 (1)	0.3338 (4)	0.043
C11	0.1931 (5)	−0.2683 (8)	0.1418 (3)	0.023
C12	0.3019 (5)	−0.2645 (8)	0.1347 (3)	0.020
C13	0.3188 (5)	−0.2157 (9)	0.0638 (3)	0.025
C14	0.2248 (5)	−0.1806 (8)	0.0276 (3)	0.023
C15	0.1471 (5)	−0.2184 (8)	0.0744 (3)	0.020
C21	0.1351 (5)	−0.3415 (9)	0.2022 (3)	0.030
C22	0.3803 (5)	−0.3467 (9)	0.1854 (4)	0.033
C23	0.4204 (6)	−0.220 (1)	0.0312 (4)	0.035
C24	0.2069 (6)	−0.122 (1)	−0.0479 (3)	0.034
C25	0.0354 (5)	−0.235 (1)	0.0536 (4)	0.029
Cp	0.237	−0.230	0.088	

[a] The isotropic equivalent displacement parameters are defined as one-third of the trace of the orthogonalized U_{ij} tensor. Cp denotes the center of the aromatic π-ligand.

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[16] Fischer, E. O.; Huttner, G.; Linder, T. L.; Frank, A.; Kreissl, F. R. *Angew. Chem.* **1976**, *88*, 228; *Angew. Chem., Int. Ed. Engl.* **1976**, *158*, 231.

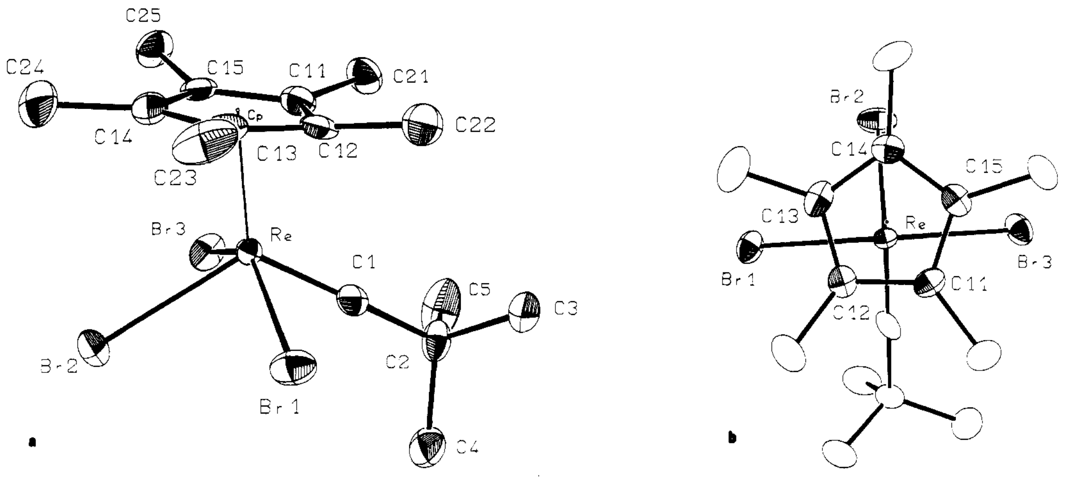


Figure 4. Two ORTEP representations of the neopentylidyne rhenium(VII) complex (η^5-C_5Me_5)$(Br)_3Re{\equiv}CC(CH_3)_3$ (**3b**): (a) side view; (b) top view. Thermal ellipsoids are at 50% probability level. Hydrogen atoms are omitted for clarity.

Table IV. Selected Bond Distances (Å) and Angles (deg) of the Neopentylidynerhenium(VII) Complex 3b[a]

	Distances		
Re–C1	175.5 (6)	Re–C15	245.4 (6)
Re–Br1	258.1 (1)	C11–C12	143.9 (8)
Re–Br2	256.9 (1)	C12–C13	142.2 (9)
Re–Br3	257.5 (1)	C13–C14	140.6 (9)
Re–C11	226.1 (6)	C14–C15	141.2 (9)
Re–C12	224.3 (6)	C15–C11	143.7 (9)
Re–C13	244.1 (6)	C1–C2	148.0 (8)
Re–C14	253.7 (6)	Re–Cp	207.0
	Angles		
Re–C1–C2	179.1 (5)	Br1–Re–Br3	144.5 (1)
C1–Re–Br1	81.4 (2)	Br1–Re–Cp	107.9
Br1–Re–Br2	80.7 (1)	Br2–Re–Cp	113.9
Br2–Re–Br3	80.9 (1)	Br3–Re–Cp	107.2
Br3–Re–C1	83.3 (2)	C1–Re–Cp	123.5
C1–Re–Br2	122.6 (2)		

[a] Cp denotes the center of the pentamethylcyclopentadienyl ligand.

(η^5-C_5Me_5)$(Br)_3Re{\equiv}CC(CH_3)_3$ (**3b**) could be obtained from acetone by standard cooling techniques. The compound exists in the crystal as discrete molecular units. There are no abnormally short intermolecular contacts. The configuration of **3b** is illustrated in Figure 4. Interatomic distances and angles are given in Table IV. The molecule exhibits a "four-legged piano stool" geometry. The Re–C1 bond length is 175.5 (6) pm, which is typical of a rhenium–carbon triple bond.[2c,7,17] The angle of 179.1 (5)° defining the Re≡C1—C2 fragment is in support of an ideal sp hybridization. The cis angles of the four monodentate ligands are quite similar (80.7–83.3°) whereas the two trans angles C1–Re–Br2 (122.6°) and Br1–Re–Br3 (144.5°) differ by 22°. The three rhenium–bromine bond lengths are all within 257.4 ± 0.6 pm, i.e., any trans influence of the alkylidyne unit to the Re–Br2 bond is lacking. However, there is a rather strong trans influence to the five-membered ring ligand. For instance the carbon atom in a "trans position" is 29 pm further from the metal than the carbon atoms C11 and C12 (Table IV). The C1–C2 distance [147.9 (8) pm] is insignificantly longer than one would expect for a "normal" C(sp)–C(sp^3) single bond. The literature value is 146 pm.[18]

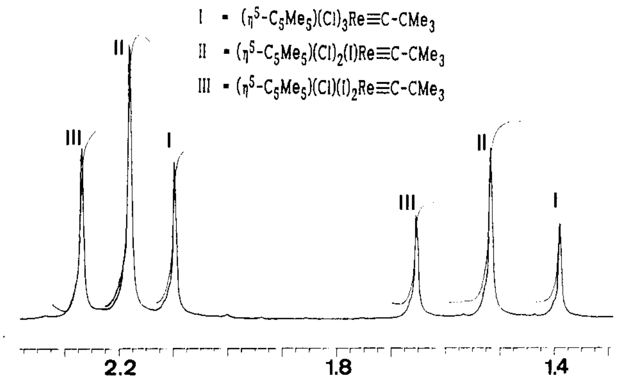
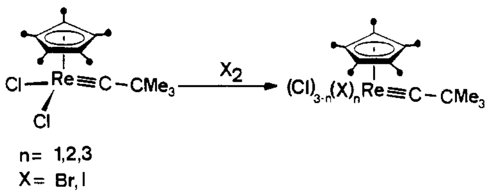


Figure 5. ^1H NMR of the oxidation of **2a** by iodine.

Scheme V. Oxidation of (η^5-C_5Me_5)$(Cl)_2Re{\equiv}CC(CH_3)_3$ with Bromine and Iodine



V. Mixed-Halogen Carbyne Complexes and Phosphane Derivatives. Oxidation of **2a** by bromine or iodine gives a mixture of the three alkylidyne complexes (η^5-C_5Me_5)$(Cl)_3Re{\equiv}CC(CH_3)_3$ (**3a**), (η^5-C_5Me_5)$(Cl)_2(X)Re{\equiv}CC(CH_3)_3$ (**3d**), and (η^5-C_5Me_5)$(Cl)(X)_2Re{\equiv}CC(CH_3)_3$ (**3e**; Scheme V) as shown by ^1H and ^{13}C NMR spectroscopy. The spectra of the "pure" compounds **3a** and **3b** are known (see above). The complex distribution is 1/2/1 by NMR (Figure 5). The existence only of isomers of **3d** can be

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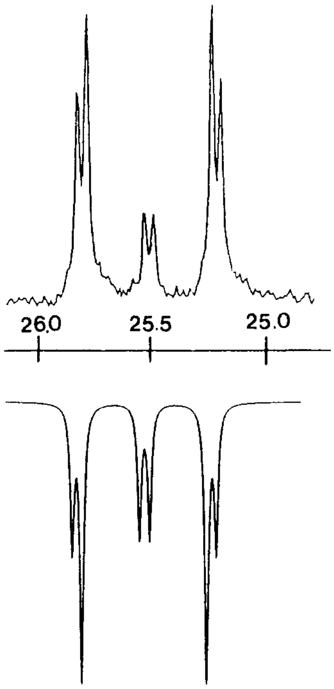

Figure 6. Experimental (top) and simulated (bottom) $P(CH_3)_3$ region of the $^{13}C\{^1H\}$ NMR spectrum of the neopentylidyne complex $[(\eta^5\text{-}C_5Me_5)\{P(CH_3)_3\}_2Re{\equiv}CC(CH_3)_3]^+[Cl]^-$ (**16**).

excluded by an EI mass spectrum. It shows in the case of X = Br as highest mass the isotope pattern of $(\eta^5\text{-}C_5Me_5)(Br)_2Re{\equiv}CC(CH_3)_3$ $[M - Cl]^+$ which cannot derive from an isomer of $(\eta^5\text{-}C_5Me_5)(Cl)_2(Br)Re{\equiv}CC(CH_3)_3$ (**3d**). A complete separation of the mixture is not possible because the solubilities are similar. If the oxidation of **2a** is carried out with a 10-fold excess of bromine, the same product distribution 1/2/1 as in the stoichiometric case is obtained. The interpretation is that primarily the expected complex **3d** is formed, which then scrambles to **3a** and **3e** via intermolecular halogen exchange. Obviously the "mixed" compounds **3d** and **3e** are thermodynamically preferred because the "pure" bromine compound $(\eta^5\text{-}C_5Me_5)(Br)_3Re{\equiv}CC(CH_3)_3$ (**3b**) is not observed. The binomial distribution and the existence of **3a** arises from stoichiometry. Stirring of $(\eta^5\text{-}C_5Me_5)(Br)_3Re{\equiv}CC(CH_3)_3$ and $(\eta^5\text{-}C_5Me_5)(Cl)_3Re{\equiv}CC(CH_3)_3$ yields a 1/1 mixture of **3d** and **3e**. The nature of the intermolecular halogen scrambling is not clear because **3** are 18-electron complexes that do not require dimerization.

Reduction of **2** to rhenium(V) compounds is effected by trimethylphosphane. Thus treatment of **2a** with 3 equiv of trimethylphosphane gives a brown solution of $[P(CH_3)_3]_3(Cl)_2Re{\equiv}CC(CH_3)_3$ (**15**) and a white precipitate of $[(\eta^5\text{-}C_5Me_5)\{P(CH_3)_3\}_2Re{\equiv}CC(CH_3)_3]^+[Cl]^-$ (**16**).[7] The analytical data of **15** and **16** are given in ref 7. In the present paper we only want to discuss the ^{13}C NMR spectrum of **16**. The peaks at δ 12.2 and 101.3 arise from the C_5Me_5 ring ligand. The *tert*-butyl group gives rise to two singlets at δ 27.3 $[C(\mathit{C}H_3)_3]$ and 55.3 $[\mathit{C}(CH_3)_3]$. The alkylidyne carbon atom appears as a low-field triplet at δ 304.1 $[^2J(C,P) = 10.0$ Hz$]$. A complex multiplet of the $P(CH_3)_3$ carbon atoms is located at δ 25.5 (Figure 6). Taking into account that $[(\eta^5\text{-}C_5Me_5)][^{31}P(^{13}CH_3)(CH_3)_2][^{31}P(CH_3)_3]Re{\equiv}CC(CH_3)_3$ is the isotopomer actually observed, the multiplet in the $P(CH_3)_3$ region can be simulated with the assumption of an AXY spin system $[^1J(C,P) = 36.0$ Hz, $^2J(C,P) = 3.3$ Hz, $^2J(P,P) = -15.7$ Hz, $\Delta P_x - \Delta P_y = 2.25$ Hz$]$.[28] A similar spectrum is described by Hoffman and Wierda for the octahedral complex $Re({=}O)(CH_3)_2(Cl)[P(CH_3)_3]_2$.[12k]

Conclusions

Mixed alkyl–chloro complexes of rhenium(V), e.g., $(\eta^5\text{-}C_5Me_5)Re(Cl)_2(CH_3)_2$, are accessible through redox-neutral chlorination of the corresponding oxo precursor species. e.g., $(\eta^5\text{-}C_5Me_5)Re({=}O)(CH_3)_2$, by means of $(\eta^5\text{-}C_5H_5)TiCl_3$ in a simple, possibly general exchange reaction $[(CH_3)_2M{=}O \rightarrow (CH_3)_2MCl_2]$. However, the success of this method depends also on the nature of the *alkyl* group(s). Thus, oxo–chlorine exchange of the bis(neopentyl) derivative entails the formation of novel rhenium(VI) carbyne complexes with concomitant elimination of neopentane $[(R_3CCH_2)_2M^V({=}O) \rightarrow R_3CC{\equiv}M^{VI}(Cl)_2]$. These compounds undergo clean one-electron oxidation to yield the corresponding diamagnetic rhenium(VII) alkylidynes. Complexes having β-hydrogen-containing alkyl groups are successfully chlorinated by the above-named method as well. An example is the diethyl complex $(\eta^5\text{-}C_5Me_5)Re(Cl)_2(C_2H_5)_2$; this compound, however, undergoes *reductive* coupling to the rhenium(IV) dimer $[(\eta^5\text{-}C_5Me_5)Re(Cl)_2(\mu\text{-}Cl)]_2$. Basically the same observation is made for the dibenzyl derivative that gives a structurally defined (μ-benzylidyne)rhenium(IV) dimer.[30] Thus alkylidyne complexes of rhenium are accessible by both oxidative and reductive processes starting at oxidation state 5+.

Experimental Section

General Techniques. All experiments were performed under prepurified nitrogen atmosphere by using standard Schlenk techniques. Solvents used in the preparations were purified by standard techniques and were dry and oxygen-free. Infrared spectra were recorded in KBr pellets with a Nicolet FT-5DX or a Beckman 4240 instrument and are reported in cm^{-1}. Silylated silica 60 (Merck No. 7719; 0.063–0.200 mm) that was heated to 200 °C for 3 days in vacuo was used for column chromatographic purification. The various NMR spectra were recorded on JEOL instruments (JMX-GX-270, JMX-GX-400). The ^1H NMR chemical shifts are reported relative to TMS, with the ^1H impurity in the solvent (benzene-d_6, δ 7.15; $CDCl_3$, δ 7.24; CD_2Cl_2, δ 5.32) as internal standard, and ^{13}C NMR chemical shifts are reported relative to the solvent signal (C_6D_6, δ 128.0; $CDCl_3$, δ 77.0; CD_2Cl_2, δ 53.8). All J values are reported in hertz. ^{31}P NMR spectra are referenced to external 85% H_3PO_4 with positive chemical shifts downfield. Mass spectra were recorded on a Varian MAT 311-A using the direct inlet method with a 70-eV ionizing radiation or on a Varian MAT FS-90 using the field desorption technique; m/z values are reported for ^{187}Re, normal $^{185/187}Re$ isotope distributions observed. Microanalyses were performed in the Mikrolaboratorium of our institute.

Preparations. (1) General Procedure for the Dialkyl Complexes $\mathbf{Cp^*Re({=}O)(R)_2}$ (1). A suspension of $Cp^*Re({=}O)(Cl)_2$ (408 mg, 1.00 mmol) in 10 mL of THF is added dropwise to a solution of 3 mmol of RMgCl in 10 mL of THF at −70 °C. After stirring for 5 min, the solution is allowed to warm to ambient temperature and is then stirred for another 60 min. The excess of Grignard reagent is destroyed by 1 equiv of water; for complexation of the $MgCl_2$ 3 mmol of 1,4-dioxane are added. The solvent is then removed in vacuo. The resulting brown residue is extracted into n-pentane, and the solution is filtered to remove $MgCl_2{\cdot}$1,4-dioxane. Finally, **1** can be purified by column chromatography on silylated silica, at 15 °C, with n-hexane acting as the eluent; yield 75%, brown needles.

(a) $\mathbf{Cp^*Re({=}O)(\eta^1\text{-}C_3H_5)_2}$ (1b): ^1H NMR ($CDCl_3$) 1.83 (s, 15, $C_5\mathit{Me}_5$), 3.06 (dddd, 2, $C\mathit{H}HCH{=}CH_2$), 3.70 (dddd, 2, $CH\mathit{H}CH{=}CH_2$), 4.72 (dddd, 2, $CH_2CH{=}C\mathit{H}H$), 5.02 (dddd, 2, $CH_2CH{=}CH\mathit{H}$), 6.42 (dddd, 2, $CH_2C\mathit{H}{=}CH_2$); coupling constants for the ABCXY spin system, $CH^1H^2CH^3{=}CH^4H^5$ (H^3 and H^5 are cis configurated) $^2J(1,2) = 11.2$, $^3J(1,5) = 8.5$, $^3J(2,5) = 7.4$, $^4J(1,3) = 0.3$, $^4J(1,4) = 1.1$, $^4J(2,3) = 1.1$, $^4J(2,4) = 1.3$, $^2J(3,4) = 2.5$, $^3J(3,5) = 9.9$, $^3J(4,5) = 16.9$. $^{13}C\{^1H\}$ NMR ($CDCl_3$) 10.3 ($C_5\mathit{Me}_5$), 13.2 ($\mathit{C}H_2CH{=}CH_2$), 98.3 (C_5Me_5), 109.1 ($CH{=}\mathit{C}H_2$), 150.5 ($\mathit{C}H{=}CH_2$). IR (KBr, cm^{-1}) $\nu(CH{=}CH_2)$ 1615 s. Anal. Calcd for

$C_{16}H_{25}ORe$: C, 45.80; H, 6.01; O, 3.81. Found: C, 45.71; H, 6.13; O, 3.28.

(b) $Cp^*Re(=O)[CH(CH_3)_2]_2$ (1h): ^1H NMR ($CDCl_3$) 1.59 (d, ^3J = 7.3, 6, CH*Me*Me), 1.76 (d, ^3J = 7.3, 6, CHMe*Me*), 1.85 (s, 15, C_5Me_5), 3.60 (sep, ^3J = 7.3, 2, C*H*Me_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 10.7 (C_5Me_5), 13.3 ($CHMe_2$), 33.1 (CH*Me*Me), 34.7 (CHMe*Me*), 99.1 (C_5Me_5). IR (KBr, Cm^{-1}) ν(Re=O) 981, 960 vs. Anal. Calcd for $C_{16}H_{29}ORe$: C, 45.37; H, 6.90; O, 3.78. Found: C, 44.93; H, 6.79; O, 3.59.

(2) $(\eta^5\text{-}C_5Me_5)Re(=O)(Cl)(CH_3)$ (7). A suspension of 440 mg (1.00 mmol) of $(\eta^5\text{-}C_5Me_5)Re(Cl)_3(CH_3)$ (10) in 20 mL of toluene was allowed to react at 25 °C with a solution of H_2O (18 μL, 1.00 mmol) and pyridine (160 μL, 2.00 mmol) in 3 mL of THF. After stirring for 2 h, the brown reaction solution was filtered (separation of the precipitated pyridinium hydrochloride) and then concentrated in vacuo. Addition of a layer of *n*-pentane results in crystallization of 350 mg (90%) of product, mp 174 °C. ^1H NMR ($CDCl_3$) 2.02 (s, 15, C_5Me_5), 2.53 (s, 3, $ReCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6) −11.0 ($ReCH_3$), 10.8 (C_5Me_5), 103.6 (C_5Me_5). IR (KBr, cm^{-1}) ν(Re=O) 963, 950 vs; ν (Re-Cl) 342 m. Anal. Calcd for $C_{11}H_{18}ClORe$: C, 34.06; H, 4.68; O, 9.14. Found: C, 33.82; H, 4.66; O, 9.95.

(3) $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_3)(R')$ (1c–e). For the preparation, see above.

(a) $R' = C_2H_5$: ^1H NMR (C_6D_6) 1.44 (s, 15, C_5Me_5), 1.94 (s, 3, $ReCH_3$), 1.95 (tr, ^3J = 7.6, 3, CH_2CH_3), 2.42 (dq, ^2J = 12.5, ^3J = 7.6, 1, C*H*HCH$_3$), 2.94 (dq, ^2J = 12.5, ^3J = 7.5, 1, CH*H*CH$_3$). ^{13}C NMR (C_6D_6) −14.2 (q, ^1J = 128.4, $ReCH_3$), 3.9 (tr, ^1J = 130.8, $ReCH_2Me$), 10.2 (q, ^1J = 127.4, C_5Me_5), 25.1 (trq, ^1J = 124.6, ^2J = 3.1, $ReCH_2Me$), 96.9 (s, C_5Me_5). EI MS (70 eV) *m/e* 382 ([M]$^+$, 35%) 337 ([Cp*ReO − 1]$^+$, 100%). IR (KBr, cm^{-1}) ν(Re=O) 969, 959, 931 vs. Mp 68 °C. anal. Calcd for $C_{13}H_{23}ORe$: C, 40.3; H, 6.08; O, 4.19. Found: C, 40.20; H, 5.95; O, 4.97.

(b) $R' = CH_2Si(CH_3)_3$: ^1H NMR (C_6D_6) 0.50 (s, 9, $SiMe_3$), 1.45 (s, 15, C_5Me_5), 1.69 (d, ^2J = 11.0, 1, C*H*HSiMe$_3$), 1.93 (s, 3, Re*Me*), 1.97 (d, ^2J = 11.0, 1, CH*H*SiMe$_3$). ^{13}C NMR (C_6D_6) −13.0 (q, ^1J = 129.5, Re*Me*), 0.0 (tr, ^1J = 119.1, CH_2SiMe_3), 1.3 (q, ^1J = 118.3, CH_2SiMe_3), 10.3 (q, ^1J = 127.8, C_5Me_5), 97.3 (s, C_5Me_5). EI MS (70 eV) *m/e* = 440 ([M]$^+$, 37%), 425 ([M − Me]$^+$, 8%), 337 ([Cp*ReO − 1]$^+$, 24%), 73 ([SiMe$_3$]$^+$, 100%). IR (KBr, cm^{-1}) ν(Re=O) 964 s; ν(Si–C) 850, 837 vs. Anal. Calcd for $C_{15}H_{29}OSiRe$: C, 40.98; H. 6.65; Re, 42.35. Found: C, 39.28; H, 6.37; Re, 43.71.

(c) $R' = CH_2C(CH_3)_3$: ^1H NMR (C_6D_6) 1.44 (s, 15, C_5Me_5), 1.52 (s, 9, CMe_3), 2.00 (s, 3, Re*Me*), 2.82 (m, 2, CH_2CMe_3). ^{13}C NMR (C_6D_6) −12.9 (q, ^1J = 128.7, Re*Me*), 10.3 (q, ^1J = 127.4, C_5Me_5), 30.8 (mult tr, CH_2CMe_3), 32.8 (non-q, ^1J = 124.1, ^3J = 4.6, CH_2CMe_3), 36.4 (dode, ^2J = 3.8, CH_2CMe_3), 97.3 (s, C_5Me_5). EI MS (70 eV) *m/e* 424 ([M]$^+$, 25%), 367 ([M$^+$ − CMe$_3$], 30%), 337 ([Cp*ReO − 1]$^+$, 100%), 57 ([CMe$_3$]$^+$, 20%). IR (KBr, cm^{-1}) ν(Re=O) 962, 952 vs. Mp 89 °C. Anal. Calcd for $C_{16}H_{29}ORe$: C, 45.37; H, 6.90; O, 3.78. Found: C, 45.51; H, 6.83; O, 3.79.

(4) Chlorination of $(\eta^5\text{-}C_5Me_5)Re(=O)(R)_2$ (1). (a) $R = CH_3$. A solution of 370 mg (1.0 mmol) of $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_3)_2$ (1f) and 220 mg (1.00 mmol) of $(\eta^5\text{-}C_5H_5)TiCl_3$ (4a) in 20 mL of toluene was stirred at room temperature for 15 h. After removing the solvent in vacuo, the residue was suspended in CH_2Cl_2 and then adsorbed on silylated silica 60. $(\eta^5\text{-}C_5Me_5)Re(Cl)_2(CH_3)_2$ (9) was eluted with toluene as a brown band; yield 250 mg (60%) of red-brown crystals: ^1H NMR (CD_2Cl_2) [T/δ[Re(CH_3)$_2$]/δ(C_5Me_5)] (−90/2.55/1.81), (−70/2.61/1.83), (−40/2.84/1.86), (±0/3.74/1.90), (20/4.69/1.93). $^{13}C\{^1H\}$ NMR (CH_2Cl_2) [T/η(C_5Me_5)/δ(ReMe_2), δ(C_5Me_5)] (−50/11.3/51.1/95.8), (25/11.8/41.2/100.0). IR (KBr, cm^{-1}) ν(Re–Cl): 325 vs, 288 m. EI MS (70 eV) *m/e* 422 ([M]$^+$, 11%), 407 ([M$^+$ − CH$_3$], 44%), 357 ([Cp*Re–Cl]$^+$, 20%), 337 ([Cp*Re − CH$_3$]$^+$, 100%). Anal. Calcd for $C_{12}H_{21}Cl_2Re$: C, 34.12; H, 5.01; Cl, 16.79. Found: C, 33.52; H, 4.89; Cl, 16.70.

(b) $R = C_2H_5$. A solution of 130 mg (0.328 mmol) of $(\eta^5\text{-}C_5Me_5)Re(=O)(C_2H_5)_2$ (1a) and 72 mg (0.328 mmol) of $(\eta^5\text{-}C_5H_5)TiCl_3$ in 5 mL of toluene was stirred for 24 h at 25 °C. The solvent was removed in vacuo, and the ^1H NMR spectrum recorded from the crude product: ^1H NMR ($CDCl_3$) 2.03 (s, 15, C_5Me_5), 2.12 (tr, ^3J = 7.3, 6, CH_2Me), 2.98 (dq, ^2J = 11.6, ^3J = 7.3, 2, C*H*HMe), 4.15 (dq, ^2J = 11.6, ^3J = 6.8, 2, CH*H*Me). If 1a and 2 equiv of **4a** are stirred at 110 °C, the reaction ends at the binuclear complex $[(\eta^5\text{-}C_5Me_5)Re(Cl)_2(\mu\text{-}Cl)]_2$ (11): ^1H NMR (CD_2Cl_2) 1.89 (s, C_5Me_5).

(c) $R = CH(CH_3)_2$. A solution of 85 mg (0.200 mmol) of $(\eta^5\text{-}C_5Me_5)Re(=O)[CH(CH_3)_2]_2$ (**1h**) and 88 mg (0.400 mmol) of $(\eta^5\text{-}C_5H_5)TiCl_3$ in 10 mL of toluene was refluxed for 16 h. The solvent was removed in vacuo, and the ^1H NMR spectrum recorded of the crude product. The product is identified as $[(\eta^5\text{-}C_5Me_5)Re(Cl)(\mu\text{-}Cl)]_2$ (**12**): ^1H NMR ($CDCl_3$) 2.02 (s, C_5Me_5).

(d) $R = CH_2C_6H_5$. A solution of 270 mg (0.519 mmol) of $(\eta^5\text{-}C_5Me_5)Re(=O)(CH_2C_6H_5)_2$ (**1g**) and 1.00 mmol of $(\eta^5\text{-}C_5H_5)TiX_3$ (4) in 15 mL of toluene was heated under reflux. After removal of the solvent in vacuo, the crude product is purified by column chromatography on silylated silica. The product $[(\eta^5\text{-}C_5Me_5)(X)Re]_2(\mu\text{-}X)(\mu\text{-}CC_6H_5)$ (14) is eluted with toluene as a brown-violet band.

$[Cp^*(Cl)Re]_2(\mu\text{-}Cl)(\mu\text{-}CC_6H_5)$ (14a): ^1H NMR ($CDCl_3$) 1.66 (s, 30, C_5Me_5), 7.12 (m, 2, C_6H_5), 7.36 (m, 3, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 9.3 (C_5Me_5), 102.7 (C_5Me_5), 127.4/128.1/128.7/157.4 (C_6H_5), 325.5 ($\equiv CC_6H_5$). EI MS (70 eV) *m/e* 838 ([M]$^+$, 100%). IR (KBr, cm^{-1}) ν(Re–Cl) 322 s, 295 w. Anal. Calcd for $C_{27}H_{35}Cl_3Re$: C, 38.68; H, 4.21; Cl, 12.69. Found: C, 38.35; H, 4.46; Cl, 13.03.

$[Cp^*(Br)Re]_2(\mu\text{-}Br)(\mu\text{-}CC_6H_5)$ (14b): ^1H NMR ($CDCl_3$) 1.82 (s, 30, C_5Me_5), 7.18 (m, 2, C_6H_5), 7.39 (m, 3, C_6H_5). EI MS (70 eV) *m/e* 972 ([M]$^+$, 2%), 571 ([Cp*(Br)$_2$Re$\equiv$CC$_6$H$_5$]$^+$, 95%), 489 ([Cp*(Br)Re$\equiv$CC$_6$H$_5$]$^+$, 100%).

(e) $R = CH_2C(CH_3)_3$. A solution of 2.4 g (5.0 mmol) of $Cp^*Re(=O)[CH_2C(CH_3)_3]_2$ (1i) and 10 mmol of $(\eta^5\text{-}C_5H_5)TiX_3$ (X = Cl, Br) in 75 mL of toluene is heated under reflux for 18 h. After removal of the solvent in vacuo, the crude product is purified by column chromatography on silylated silica. $(\eta^5\text{-}C_5Me_5)(X)_2Re{\equiv}CC(CH_3)_3$ (2) is eluted with *n*-hexane as blue (X = Cl) or green band (X = Br). The eluate is concentrated in vacuo to 150 mL and cooled to −78 °C to afford crystals of **2**; yield 1.50 g (X = Cl)/1.80 g (X = Br) (65%).

The iodo complex **2c** can be prepared in the same way, but purification is difficult. A better way is to stir a solution of 1.0 mmol of **2a** with 450 μL (3.0 mmol, 50% excess) of iodotrimethylsilane in CH_2Cl_2 at ambient temperature for 20 h. Finally the solution is adsorbed on silylated silica and purified by column chromatography on the same material. **2c** is developed with *n*-hexane as a brown band, yield 260 mg (40%).

2a (X = Cl): EI MS (70 eV) *m/e* 461 ([M]$^+$, 55%), 355 ([Cp*ReCl − 2]$^+$, 100%). IR (KBr, cm^{-1}) ν(Re–Cl) 320, 310 s. Anal. Calcd for $C_{15}H_{24}Cl_2Re$: C, 39.04; H, 5.24; Cl, 15.37; Re, 40.35. Found: C, 38.53; H, 5.06; Cl, 15.49; Re, 41.04. ESR (toluene) sextet ($I = {}^5/_2$; $^{185/187}$Re), $\langle g \rangle$ = 2.053; $\langle A \rangle$ = 218 × 10^{-4} cm^{-1}; cyclovolt E_{ox} = 677 mV, E_{red} = −848 mV, $I_{pc}(ox)/I_{pa}(ox)$ = 1.00; $I_{pc}(red)/I_{pa}(red)$ = 1.20 (CH_2Cl_2 solution, vs Ag/AgCl). Vapor pressure osmometry (benzene) found 434, calcd 461.5.

2b (X = Br): EI MS (70 eV) *m/e* 551 ([M]$^+$, 86%), 469 ([Cp*(Br)Re$\equiv$CC(CH$_3$)$_3$]$^+$, 36%), 399 ([Cp*ReBr − 2]$^+$, 100%). Anal. Calcd for $C_{15}H_{24}Br_2Re$: C, 32.74; H, 4.40; Br, 29.04. Found: C, 32.06; H, 4.42; Br, 29.22. ESR (toluene) sextet ($I = {}^5/_2$; $^{185/187}$Re), $\langle g \rangle$ = 2.074, $\langle A \rangle$ = 196 × 10^{-4} cm^{-1}; cyclovolt E_{ox} = 643 mV, E_{red} = −855 mV; $I_{pc}(ox)/I_{pa}(ox)$ = 0.98; $I_{pc}(red)/I_{pa}(red)$ = 1.60 (CH_2Cl_2 solution; vs Ag/AgCl).

2c (X = I): EI MS (70 eV) *m/e* 645 ([M]$^+$, 100%), 517 ([M − HI]$^+$, 23%), 447 ([Cp*ReI − 2]$^+$, 44%). Anal. Calcd for $C_{15}H_{24}I_2Re$: C, 27.96; H, 3.75; I, 39.39. Found: C, 27.92; H, 3.75; I, 39.38. Cyclovolt E_{ox} = 629 mV, E_{red} = −735 mV; $I_{pc}(ox)/I_{pa}(ox)$ = 0.95; $I_{pc}(red)/I_{pa}(red)$ = 1.20 (CH_2Cl_2 solution; vs Ag/AgCl).

(5) Oxidation of $(\eta^5\text{-}C_5Me_5)(X^1)_2Re{\equiv}CC(CH_3)_3$ (2) with Halogens (X_2^2). To a solution of 1.0 mmol of $(\eta^5\text{-}C_5Me_5)(X^1)_2Re{\equiv}CC(CH_3)_3$ (2) in 15 mL of CCl_4 0.55 mmol (10% excess) of a halogen (X^2_2; or $C_6H_5ICl_2$ as chlorinating reagent) was added at ambient temperature. A precipitate occurred spontaneously. The compound $(\eta^5\text{-}C_5Me_5)$ $(X^1)_2(X^2)Re{\equiv}CCMe_3$ (3) thus formed in quantitative yield was washed three times with *n*-pentane and then dried in vacuo. Table V contains NMR data for **3**.

(a) $X^1 = X^2$ = Cl (3a): yellow powder. ^1H NMR ($CDCl_3$) 1.41 (s, 9, CMe_3), 2.11 (s, 15, C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 12.3 (C_5Me_5), 27.2 (CMe_3), 57.7 (CMe_3), 121.3 (C_5Me_5), 373.8 (Re$\equiv$C). IR (KBr, cm^{-1}) ν(Re–Cl) 320, 310 s. Anal. Calcd for $C_{15}H_{24}Cl_3Re$: C, 36.25; H, 4.87; Cl, 21.40. Found: C, 35.87; H, 4.98; Cl, 19.95.

(b) $X^1 = X^2$ = Br (3b): orange powder. ^1H NMR ($CDCl_3$) 1.49 (s, 9, CMe_3), 2.15 (s, 15, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 12.8

Table V. NMR Data ($CDCl_3$) of Compounds (η^5-C_5Me_5)(X^1)$_n$(X^2)$_{3-n}$Re$\equiv$CC(CH_3)$_3$ (n = 0–3)

	^{1}H NMR ($CDCl_3$)		$^{13}C\{^1H\}$ NMR ($CDCl_3$)				
(X^1)(X^2)	C*Me*$_3$	C_5*Me*$_5$	C_5*Me*$_5$	C*Me*$_3$	*C*Me$_3$	*C*$_5$Me$_5$	Re$\equiv$*C*
Cl_3	1.41	2.11	12.3	27.2	57.7	121.3	373.8
Cl_2Br	1.44	2.12	12.5	27.3	58.0	119.6	373.6
$ClBr_2$	1.48	2.14	12.7	27.4	58.3	118.0	373.6
Br_3	1.49	2.15	12.8	26.9	58.7	117.8	371.8
Cl_2I	1.54	2.20	13.2	27.8	58.4	117.0	368.4
ClI_2	1.67	2.28	14.2	28.6	59.2	114.1	363.6
I_3[b]	1.63	2.35	14.8	27.6	nf[a]	113.7	nf[a]

[a] Not found. [b] CD_2Cl_2.

(C_5*Me*$_5$), 26.9 (C*Me*$_3$), 58.7 (*C*Me$_3$), 117.8 (*C*$_5$Me$_5$), 371.8 (Re$\equiv$*C*). FD MS 630 ($[M]^+$, 100%), 551 ($[M - Br]^+$, 60%). Anal. Calcd for $C_{15}H_{24}Br_3Re$: C, 28.59; H, 3.84; Br, 38.04. Found: C, 28.13; H, 3.82; Br, 37.14.

X^1 = X^2 = I (3c): orange powder. ^{1}H NMR (CD_2Cl_2) 1.63 (s, 9, C*Me*$_3$), 2.35 (s, 15, C_5*Me*$_5$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 14.8 (C_5*Me*$_5$), 27.6 (C*Me*$_3$), 113.7 (*C*$_5$Me$_5$). Peaks in the NMR spectra are very broad. **3c** is not very good soluble in CH_2Cl_2, and therefore the quarternary carbon atoms are not found. Anal. Calcd for $C_{15}H_{24}I_3Re$: C, 23.37; H, 3.14; I, 49.39. Found: C, 23.49; H, 3.17; I, 48.00.

(6) Reduction of (η^5-C_5Me_5)(X)$_2$Re$\equiv$CC(CH_3)$_3$ (2) with Trimethylphosphane. Trimethylphosphane (3 mmol, 310 μL) was added to a solution of 1.00 mmol of **2** in 10 mL of toluene at −78 °C. Warming to 25 °C results in a brown solution of $[P(CH_3)_3]_3(X)_2Re{\equiv}CCMe_3$ (**15**) and a white–yellow precipitate of $[(\eta^5\text{-}C_5Me_5)[P(CH_3)_3]_2Re{\equiv}CC(CH_3)_3]^+[X]^-$ (**16**). After stirring for 1 h at 25 °C, the solution of **15** was filtered and then purified by chromatography on silylated silica. **15** was eluted with toluene as a narrow brown band. **16** was extracted with THF/CH_2Cl_2 (10/1) from the residue.

(a) $[(\eta^5\text{-}C_5Me_5)[P(CH_3)_3]_2Re{\equiv}CC(CH_3)_3]^+[Cl]^-$: ^{1}H NMR ($CDCl_3$) 1.05 (s, 9, C*Me*$_3$), 1.75 (vd, N = 9.2, 18, P*Me*$_3$), 1.99 (s, 15, C_5*Me*$_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) 12.2 (s, C_5*Me*$_5$), 25.5 [m, ^1J(C,P) = 36.0, ^2J(C,P) = 3.3, ^2J(P,P) = −15.7; $\Delta P_x - \Delta P_y$ = 2.25, P*Me*$_3$], 27.3 (s, C*Me*$_3$), 55.3 (s, *C*Me$_3$), 101.3 (s, *C*$_5$Me$_5$), 304.1 [tr, ^2J(C,P) = 10.0, Re$\equiv$*C*]. $^{31}P\{^1H\}$ NMR ($CDCl_3$) −32.0 (s, *P*Me$_3$). FD MS, m/e 544 ($[Cp^*[P(CH_3)_3]_2Re{\equiv}CC(CH_3)_3 + 1]^+$, 40%, 502 ($[M - P(CH_3)_3]^+$, 100%). Anal. Calcd for $C_{21}H_{42}Cl_2PRe$: C, 43.63; H, 7.32; Cl, 6.13; P, 10.71. Found: C, 42.00; H, 7.08; Cl, 7.07; P, 10.65.

(b) $[(\eta^5\text{-}C_5Me_5)[P(CH_3)_3]_2Re{\equiv}CC(CH_3)_3]^+[Br]^-$: ^{1}H NMR ($CD_2Cl_2$) 1.10 (s, 9, C*Me*$_3$), 1.77 (vd, N = 9.2, 18, P*Me*$_3$), 2.03 (s, 15, C_5*Me*$_5$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 12.4 (s, C_5*Me*$_5$), 25.7 (m, P*Me*$_3$), 27.5 (s, C*Me*$_3$), 55.6 (s, *C*Me$_3$), 101.9 (s, *C*$_5$Me$_5$), 304.7 [tr, ^2J(C,P) = 10.0, Re$\equiv$*C*]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) −32.2 (s, PMe$_3$).

(c) $[P(CH_3)_3]_3(Cl)_2Re{\equiv}CC(CH_3)_3$: ^{1}H NMR ($CDCl_3$) 1.13 (s, 9, C*Me*$_3$), 1.69 (v tr, N = 15.4, 18, *trans*-P*Me*$_3$), 1.73 [d, ^2J(H,P) = 8.8, P*Me*$_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) 18.9 (v tr, N = 31.4, *trans*-PMe$_3$), 25.6 [d, ^1J(C,P) = 34.2, P*Me*$_3$], 27.7 (s, C_5*Me*$_5$), 52.6 (s, *C*Me$_3$), 279.3 [q, ^2J(C,P) = 13.5, Re$\equiv$*C*]. $^{31}P\{^1H\}$ NMR ($CDCl_3$) −19.7 [d, ^2J(P,P) = 12.7, 2 P, *trans-P*Me$_3$], −21.9 [tr, ^2J(P,P) = 12.7, 1 P, *P*Me$_3$]. FD MS, m/e 554.2 ($[M]^+$, 100%).

Crystal data of compounds **1e** and **3b** together with details of the X-ray diffraction procedures are reported in Table VI. The data collection for **1e** was performed on an Enraf-Nonius CAD4 four-cycle diffractometer equipped with graphite-monochromated Mo Kα radiation. Cell dimensions were obtained from a least-squares refinement using a set of 50 reflections in the range of 33.8° < 2θ < 42.1°. Scattering factors and anormal dispersion parametes were taken from ref 25. During data collection deorientation of the crystal was controlled every 200 reflections. The intensity data were corrected for Lorentz and polarization effects and a decay of 37%. A numerical absorption correction was applied. From patterson maps the Re position could be determined. All remaining non-hydrogen atoms were located by successive structure factor calculations and difference Fourier maps. The least-squares full-matrix refinement minimized the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Hydrogen atoms were calculated in ideal positions (C–H = 95 pm) and added to the calculations with collective isotropic temperature factors; however, they were not refined. The refinement converged with unweighted and weighted agreement factors R = 0.065 and R_w = 0.039, respectively. For a satisfactory, complete analysis, the criterion was the absence of significant features in the final difference map.

Table VI. Crystal Data Summary for 1e and 3b

	1e	**3b**
	Crystal Parameters	
Empirical formula	$C_{16}H_{29}ORe$	$C_{15}H_{24}Br_3Re$
formula wt	423.6	630.3
color of cryst/shape	brown plates	brown prisms
cryst size, mm	0.65 × 0.03 × 0.55	0.77× 0.13 × 0.08
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
temp, °C	23 ± 1	−50 ± 3
a, pm	960.7 (2)	1311.5 (2)
b, pm	2844.5 (4)	723.0 (1)
c, pm	1260.7 (2)	1901.6 (2)
V, pm^3	3445×10^6	1801×10^6
β, deg		92.68 (1)
Z, molecules/cell	8	4
ρ_{calc}, [g/cm^3]	1.633	2.324
wavelength, pm	71.07 (Mo Kα)	71.07 (Mo Kα)
μ(Mo Kα), cm^{-1}	71.4	129.8
	Data Collection	
diffractometer	Enraf-Nonius CAD4	Syntex $P2_1$
scan type	ω-scan	ω-scan
θ range, deg	1.0–25.0	1.5–26
max scan time, s	90	70
scan width, deg	(2.00 + 0.25 tan θ)	0.80
total no. of reflns coll	3452	4017
no. of unique reflns	2430	3525
	Refinement	
solution	Patterson	Patterson
hydrogen atoms	not refined	not refined
refinement	full-matrix least-squares	
minimization function	$\sum w(\|F_o\| - \|F_c\|)^2$	
weighting scheme	$w = 1/\sigma^2(F_o)$	
no. of reflns included	$2054/I > 1.0$	$3517/I > 0.0$
no. of params refined	163	172
R[a]	0.065	0.040
R_w[b]	0.039	0.034
goodness of fit (GOF)[c]	3.742 (ρ = 0.00)	*d*
shift/err	0.00	0.00
max e_0/Å^3 (57 pm near Re)	3.22	0.93
min e_0/A^3 (82 pm near Re)	−2.37	−1.17

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$. [d] Not supported by the Programm SHELX76.

Data for **3b** were collected on a Syntex $P2_1$ diffractometer. No decay of the intensity check reflections was observed. For calculation of cell parameters, absorption correction, manipulation of data, and refinement of structure see above and Table VI. All calculations were performed by VAX-11/730 and VAX-8200 computers using the STRUX-II program system with the programs SDP, ORTEP, PARAM, SHELX-76, and SHELX-86.[19-24,26-29] Selected bond

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lengths are given in Tables II and IV.

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Supplementary Material Available: Tables of the anisotropic thermal parameters of the non-hydrogen atoms and of the fractional coordinates, including the calculated hydrogen atoms, and full listings of bond lengths and angles of compounds **1e** and **3b** (17 pages); listings of observed and calculated structure factors for **1e** and **3b** (34 pages). Ordering information is given on any current masthead page.

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Reaction of Organoisothiocyanates with [Co(η-C$_5$H$_5$)(PPh$_3$)$_2$]. Preparation, Structure, and Reactivity of Trinuclear Cobalt Complexes Containing a Triply Bridging, Two-Electron-Donor CNR Ligand

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The slow addition of RNCS to [Co(η-C$_5$H$_5$)(PPh$_3$)$_2$] in benzene at room temperature gives a good yield of green [Co$_3$(η-C$_5$H$_5$)$_3$(μ_3-S)(μ_3-CNR)] (**1**) where R = alkyl or aryl. A crystal structure determination (R = Et; monoclinic, space group $P2_1/c$ with a = 14.405 (4) Å, b = 9.221 (3) Å, c = 15.040 (5) Å, β = 117.9 (3)°, and Z = 4) shows that these complexes contain a planar Co$_3$(η-C$_5$H$_5$)$_3$ triangle (Co–Co = 2.447, 2.452, and 2.483 (1) Å) capped on one side by a μ_3-S atom and on the other by a μ_3-CNR ligand acting as a two-electron donor through C. The CNEt ligand is bent at N so that the N–Et bond lies above the center of one Co–Co bond with a C–N–Et angle of 129°. The N atoms of **1** are basic, but the basicity is a function of R. When R = Me or Et (**1**) reacts with [Ph$_3$C]BF$_4$ to give [Co$_3$(η-C$_5$H$_5$)$_3$(μ_3-S){μ_3-CN(H)R}]BF$_4$, [**2**]BF$_4$, although the source of the protons is unclear, and with MeI or R′SO$_3$CF$_3$ to give [Co$_3$(η-C$_5$H$_5$)$_3$(μ_3-S){μ_3-CN(R′)R}]X, [**3**]X; both [**2**]BF$_4$ and [**3**]X react with excess HBF$_4$·OEt$_2$ to give [Co$_3$(η-C$_5$H$_5$)$_3$(μ_3-S){μ_3-CN(H)$_2$R}][BF$_4$]$_2$, [**4**][BF$_4$]$_2$, and [Co$_3$(η-C$_5$H$_5$)$_3$(μ_3-S){μ_3-CN(H)(R′)R}][BF$_4$]$_2$, [**5**][BF$_4$]$_2$ salts, respectively. In contrast, when R = aryl, both [Ph$_3$C]BF$_4$ and excess HBF$_4$·OEt$_2$ convert **1** to [**2**][BF$_4$] only, and some **1** molecules are not alkylated to [**3**]I by MeI, but all are alkylated by MeSO$_3$CF$_3$. Infrared and NMR spectroscopic data are reported and discussed.

Introduction

CO can act as a two-electron-donor ligand that coordinates through carbon to one, two, or three metal atoms simultaneously. CS acts similarly.[4,5] Prior to the preliminary report of this work,[6] CNR ligands had been observed to coordinate only as a two-electron donor through carbon to one or two metal atoms.[4] A possible exception is [Cr(CO)$_5$CNCCo$_3$(CO)$_9$],[7] but this is best thought of as [Cr(CO)$_5$CNR] where R = CCo$_3$(CO)$_9$.

As [Co(η-C$_5$H$_5$)L$_2$] complexes (L = CO or PR$_3$) cleave carbon disulfide giving [Co$_3$(η-C$_5$H$_5$)$_3$(μ_3-S)(μ_3-CS)],[5,8] it seemed reasonable to anticipate that a similar reaction with organoisothiocyanates, RNCS, would lead to [Co$_3$(η-C$_5$H$_5$)$_3$(μ_3-S)(μ_3-CNR)] with triply bridging organoisocyanide ligands. The route has proved successful, and we describe here a series of such complexes together with their reactions with various Lewis acids that convert the μ_3-CNR ligands to [μ_3-CN(R′)R]$^+$ and [μ_3-CN(R′)$_2$R]$^{2+}$ ligands. The [μ_3-CNMe$_2$]$^+$ and [μ_3-CN(H)Me$_2$]$^{2+}$ ligands have been reported previously in [Co$_3$(CO)$_9$CNMe$_2$] and [Co$_3$(CO)$_9$CN(H)Me$_2$][PF$_6$].[9]

Experimental Section

Organoisothiocyanates were prepared by standard methods[10] or purchased and distilled prior to use. [Co(η-C$_5$H$_5$)(PPh$_3$)$_2$] was prepared as described[11] and used in situ. Other chemicals were purchased.

All reactions were carried out in purified solvents at room temperature under an atmosphere of nitrogen unless it is stated otherwise.

Infrared spectra were run on Perkin-Elmer 1710 FTIR or 283B spectrometers. NMR spectra were run on a JEOL JNM-GX270 spectrometer using Me$_4$Si as an internal standard.

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