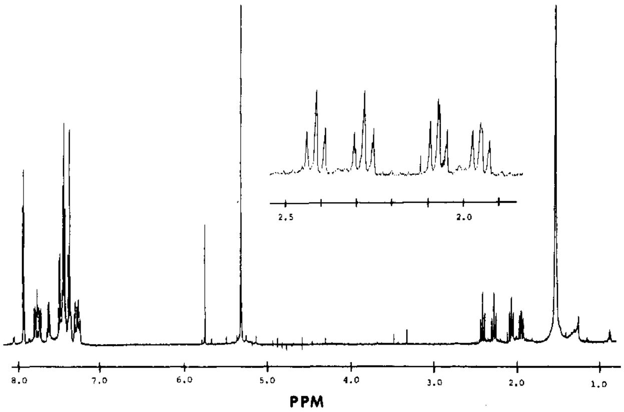

Figure 2. The 500-MHz ^1H NMR spectrum of the $CHNO_2$-bridged complex in CD_2Cl_2. The insert contains the CH_2 region with both ^{31}P and ^1H coupling to each hydrogen atom.

formation of the A-frame species. Disorder of the NO_2 group (occupancy about 1:1) left some uncertainty with regard to the constitution of the bridge. Therefore a proton NMR spectrum at 500 MHz in CD_2Cl_2 was obtained.[12] The four observed 3-line resonances (Figure 2) in the CH_2 region (1.8–2.5 ppm) and the single uncoupled resonance at 5.75 ppm unequivocally establish the presence of the unsymmetrical $CHNO_2$ bridge. Integration verifies the 8:1 intensity ratio expected for this structure.

The geometry about each gold(III) atom is typical of an A-frame species with a Au⋯Au separation of 3.073 (1) Å. A Au–Au distance of ~2.6 Å is obtained generally for **2**, X = Cl, Br, I, $SC(S)N(C_2H_5)_2$, SC(O)Ph, etc. Thus Au–Au bond rupture occurs during the formation of **3**. This must be accompanied by some chemical reduction of either **2** or the CH_3NO_2 solvent itself. Studies underway are directed to a resolution of this question. No H_2 evolution has been detected, although its formation cannot yet be ruled out conclusively.[13]

Acknowledgment. The National Science Foundation, CHE-83-05046, has supported this work. Partial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation also is acknowledged. H.C.K. was the recipient of a NSF summer fellowship for college teachers.

Registry No. 1, 81457-56-9; 2 (X = $OC(O)C_6H_5$), 90990-50-4; 2 (X = $SC(O)C_6H_5$), 90968-87-9; 3, 90968-88-0; CH_3NO_2, 75-52-5; benzoyl peroxide, 94-36-0; dibenzoyl disulfide, 644-32-6.

Supplementary Material Available: Tables of atom coordinates (Table I), bond lengths (Table II), bond angles (Table III), isotropic temperature factors (Table IV), hydrogen atom coordinates (Table V), and observed and calculated structure factors (Table VI) (24 pages). Ordering information is given on any current masthead page.

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[11] Crystallographic data: $C_{43}H_{39}Au_2NO_6P_2$; monoclinic, space group $P2_1/n$ (No. 14); a = 10.7806 (14) Å, b = 17.643 (2) Å, c = 21.739 (3) Å, β = 101.351 (11)°, Z = 4, 3158 unique reflections with $I \geq 3\sigma(I)$. With 338 parameters R = 0.0391, R_w = 0.0397, and goodness of fit = 1.179; maximum shift/error = 0.008. Data collected on Nicolet P3F diffractometer at ambient temperature with graphite-monochromated Mo Kα radiation. Data corrected for Lorentz, decay, polarization, and absorption effects. All calculations were performed with SHELXTL crystallographic programs.

[12] We wish to thank Professor Ian Scott and Dr. Paul Fagerness, Center for Biological NMR, Texas A&M University, for these measurements.

[13] Note added in proof. The UV–vis spectrum changes observed during the reaction suggest the presence of at least three gold-containing species.

(Pentamethylcyclopentadienyl)trioxorhenium, $(\eta^5\text{-}C_5Me_5)ReO_3$

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Summary: $(\eta^5\text{-}C_5Me_5)ReO_3$ has been synthesized from the reaction of $(\eta^5\text{-}C_5Me_5)Re(CO)_2(THF)$ with O_2 at 450 psi. It is a rare example of a group 7A organometallic compound having the metal in the maximum group oxidation state *and* an 18-electron configuration.

One aspect of the use of pentamethylcyclopentadienyl ligands that has recently been given attention is the ability to stabilize higher formal oxidation states in organometallic complexes.[1] We here wish to report an extreme instance of this in the synthesis of the air-stable rhenium(VII) complex $(\eta^5\text{-}C_5Me_5)ReO_3$. It will be noted coincidentally that despite the maximum group oxidation state being achieved this is nevertheless an 18-electron complex. In the VI and VII oxidation states for rhenium, the occurrence of metal–carbon bonds is very rare indeed and is limited largely to the methyls $ReMe_6$,[2,3] Me_4ReO,[4] Me_3ReO_2,[3] and $MeReO_3$.[5] Conversely, cyclopentadienyl- or (pentamethylcyclopentadienyl)rhenium compounds are numerous[6] but are typically found with low oxidation states.

$(\eta^5\text{-}C_5Me_5)ReO_3$ (**1**) was first observed by us serendipitously in an attempt to replace the MeCN ligand in $[(\eta^5\text{-}C_5Me_5)Re(CO)(MeCN)(p\text{-}N_2C_6H_4OMe)]^+$[7] with dinitrogen and was identified readily from its elemental analysis and IR, mass, and ^1H NMR spectra. The MeCN complex in THF was pressurized with 1500 psi of undeoxygenated nitrogen for 3 days. IR spectroscopy then showed the absence of any carbonyl complexes, and **1** was isolated after chromatography on neutral alumina as the only rhenium compound that eluted. It was similarly produced as a coproduct in the synthesis of $(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)$ from $(\eta^5\text{-}C_5Me_5)Re(CO)_2(THF)$ in THF also using undeoxygenated nitrogen at 1500 psi of pressure. Reaction of these carbonyl complexes with dioxygen impurity in the dinitrogen was implicated and was confirmed by the direct synthesis of **1** in 55% yield from $(\eta^5\text{-}C_5Me_5)Re(CO)_2(THF)$[8] in THF under 450 psi of dioxygen for 1 day. Chromatography on silica gel first eluted organic products (see below) using hexane and then a yellow band of **1** using ether, which was recrystallized as yellow needles that melt without decomposition at 192 °C.[9]

The spectroscopic properties of **1** are simple indeed and in agreement with its formulation as a mononuclear complex as illustrated. The 70-eV electron-impact mass spectrum gave the parent ion isotopic cluster in close to

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[1] For leading references see: Tilley, D. T.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274. Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470. Maitlis, P. M. *Coord. Chem. Rev.* **1982**, *43*, 377.

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[5] Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.

[6] Annual reviews of π-cyclopentadienyl compounds are to be found in: *Organomet. Chem.* **1983**, *11*, and previous volumes.

[7] Barrientos, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D., submitted for publication in *Organometallics*.

[8] Synthesized in situ by UV irradiation of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ in THF. The tricarbonyl itself in THF was observed not to react in 3 days with O_2 under the same conditions (450 psi).

[9] Anal. Calcd for $(\eta^5\text{-}C_5Me_5)ReO_3$: C, 32.43; H, 4.05. Found: C, 32.31; H, 3.95.

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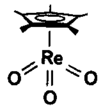

theoretical abundancies as the only prominent feature, with m/z values (theoretical percent in parentheses): 368 [56% (58.5%), ^{185}Re], 369 [8% (6.7%)], 370 [100% (100%), ^{187}Re], 371 [12.5% (11.5%)]. The IR spectrum (KBr) had bands at 910 (s) cm^{-1} [$\nu_{\mathrm{sym}}(\mathrm{ReO_3})$] and 881 (vs) cm^{-1} [$\nu_{\mathrm{asym}}(\mathrm{ReO_3})$], and the ^{1}H NMR (CDCl$_3$) had only a single resonance for the C$_5$Me$_5$ group at δ 2.16. It sublimes readily at 40 °C and 10^{-2} torr and is insoluble in hexane but soluble in common organic solvents (ether, THF, C$_6$H$_6$, MeOH, CH$_2$Cl$_2$), and the solutions are air stable. Although optically excellent crystals can be grown readily from, e.g., CH$_2$Cl$_2$–hexane, all thus far examined have been twinned and no X-ray structure is yet available.

In all of the reactions giving 1 (above) where THF is the solvent, organic oxidation products are observed, identified by a characteristic IR having prominent absorptions at 1776 (vs) and 1726 (m) cm^{-1} plus associated shoulders. These separate from 1 by elution in hexane, and GC/MS shows there to be at least five components, not all yet identified. The major one is γ-butyrolactone (ν(CO) 1776 cm^{-1}; m/z 86). These oxidation products were not formed when pure THF was pressurized with O$_2$ at 450 psi for 1 day alone or in the presence of 1.

Acknowledgment. This work was supported by N.S.E.R.C. Canada through an operating grant to D.S. We are grateful to the Universidad Catolica de Valparaiso, Chile, for leave of absence for A.H.K.-O.

Registry No. 1, 90695-83-3; (η^5-C$_5$Me$_5$)Re(CO)$_2$(THF), 90695-84-4.

Preparation of Novel Ruthenium(IV) Complexes (η^5-C$_5$(CH$_3$)$_5$)Ru(η^3-allyl)X$_2$ and (η^5-C$_5$H$_5$)Ru(η^3-allyl)X$_2$ by Oxidative Addition of Allylic Halides to Ruthenium(II) Precursors

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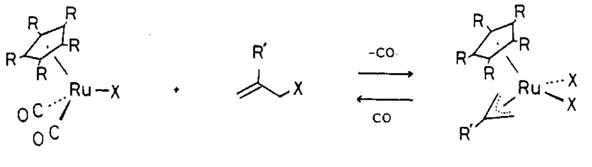
Summary: Oxidative addition of allylic halides to ruthenium(II) carbonyl complexes Cp′Ru(CO)$_2$X and CpRu(CO)$_2$X [Cp′ = η^5-C$_5$(CH$_3$)$_5$; Cp = η^5-C$_5$H$_5$; X = Br, Cl] resulted in the formation of novel Ru(IV) complexes Cp′Ru(η^3-allyl)X$_2$ and CpRu(η^3-allyl)X$_2$. Reaction of the resulting ruthenium(IV) allyl complexes with CO did not lead to incorporation of CO into the allylic moiety but gave rise to reductive elimination of the allylic halides from the Ru(IV) metal center to afford the ruthenium(II) carbonyl complexes Cp′- and CpRu(CO)$_2$X.

The chemistry of late transition metals in their higher oxidation states requires further investigation.[1–3] Recent studies by Maitlis[2] and Bergman[3] have resulted in the successful preparation of several d^4 complexes of Rh(V) and Ir(V). In this context, the isoelectronic Ru(IV) complexes are an attractive target for us, only a few organometallic complexes of Ru(IV) having been reported.[4–7] In this paper, we wish to report a simple preparation of novel ruthenium(IV) π-allyl complexes by oxidative addition of allylic halides to ruthenium(II) carbonyl precursors. The resulting Ru(IV) complexes undergo smooth reductive elimination of the allylic halides by reaction with CO (Scheme I).

Scheme I



R = CH$_3$, H, R′ = Ph, CH$_3$, H, X = Br, Cl

Some Ru(IV) complexes have been prepared by oxidative addition of hydrogen,[4] halogens,[5] or quinones[6] to several Ru(II) complexes. Alternatively, oxidative cyclization of 1,3-dienes on Ru(II) species generated in situ in an alcoholic solution of RuCl$_3$ affords some ruthenium(IV) bis(π-allyl) complexes.[7] Organic halides are potentially applicable as the addenda of oxidative addition to Ru(II) precursors, but few studies have been undertaken. We have found that ruthenium(II) carbonyl complexes Cp′Ru(CO)$_2$Br (1) reacted with allyl bromide at 100–140 °C to give a new Ru(IV) complex, Cp′Ru(η^3-allyl)Br$_2$ (**5a**), in higher than 90% yields. In a typical example, a solution of 1 (372 mg, 1 mmol) in decane (10 mL) containing allyl bromide (0.17 mL, 2 mmol) was heated at 140 °C for 10 h under nitrogen. Brown crystals that precipitated from the solution were collected and were recrystallized from dichloromethane–ether to give **5a**[8] as thermally air-stable crystals. Oxidative addition of allylic halides to Cp′Ru(CO)$_2$Br (1), Cp′Ru(CO)$_2$Cl (2), CpRu(CO)$_2$Br (3), and CpRu(CO)$_2$Cl (4) can be generally used for the preparation of the ruthenium(IV) η^3-allyl complexes **5b–h** with similar procedures to that described above. The results are summarized in Table I.[9]

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[1] Organometallic compounds of Pt(IV) are well-known examples of this issue; Hartley, F. R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, p 471.

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[8] Spectral data of **5a**: ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.74 (s, 15 H, Cp′), 2.25 (d, J = 9.91 Hz, 2 H, syn proton on terminal carbon of π-allyl), 4.25 (d, J = 6.08 Hz, 2 H, anti proton on terminal carbon of π-allyl), 5.20 (m, 1 H, proton on central carbon of π-allyl); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 9.6 (q), 64.8 (d), 96.2 (d), 103.7 (s); mp 200–205 °C dec. Anal. Calcd for C$_{13}$H$_{20}$Br$_2$Ru; C, 35.72; H, 4.61. Found: C, 35.53; H, 4.56. The Ru(IV) complexes **5b–h** had satisfactory spectral data and elementary analysis. The data are given in the supplementary material.

[9] Ruthenium(II) phosphine complexes CpRu(PPh$_3$)$_2$Cl and Cp′Ru(CO)(PPh$_3$)Br also underwent the oxidative addition of allylic halides to form the corresponding ruthenium(IV) η^3-allyl complexes **5** but in 40–50% yields.