

Figure 7. First reduction potential vs number of aromatic rings for selected hydrocarbons.

and -1.7 V by CV (Figure 6a) and DPP (Figure 6b). The values of the DPP peak potentials (vs. SCE) for the purified samples are -512 , -900 , and -1382 mV for C_{60} and -516 , -888 , and -1304 mV for C_{70} . Under our experimental conditions the ferrocene/ferrocenium redox potential is $+394$ mV. Irreversible reductions are observed for C_{60} at -1514 mV and at lower potentials. Unlike C_{60} , a major reduction process starts at about -1600 mV for C_{70} . No oxidation waves are observed up to $+1000$ mV for either molecule.

These results demonstrate the reversible formation of relatively stable C_n^- , C_n^{2-} , and C_n^{3-} ($n = 60, 70$) anions in solution.²⁹ While the differences between the first and second half-wave potentials of C_{60} and C_{70} are within experimental uncertainty, the 78-mV difference between their third reduction potentials appears to be significant. The differences between the redox potentials of C_{60} relative to C_{70} indicate that it is easier to add electrons to the C_{70} dianion compared to its C_{60} counterpart. This observation is consistent with a simple charge separation delocalization model. Since C_{70} presumably is larger than C_{60} , adding electrons to the anions would be easier if the negative charges are separated by larger distances or if they can be delocalized over a large number of carbon atoms. Interestingly, the first redox potentials of C_{60}

(29) Similar results are obtained when tetrahydrofuran, sodium tetraphenyl borate, or platinum button electrodes are used.

and C_{70} are higher than those known for other aromatic hydrocarbons (see Figure 7) in qualitative agreement with the observation that the redox potential increases with the number of aromatic carbon rings.

The observation that three electrons can be added reversibly to C_n clusters is somewhat at odds with the theoretical prediction that C_{60} will add at most one electron.³⁰ Theoretical calculations however clearly indicate a triply degenerate LUMO,^{3,18,31} which suggests to us that at least 3 electrons should be added relatively easily. A more quantitative description of the orbitals in doubly and triply charged anions should be helpful. It is worth mentioning in this context that C_n species containing up to three potassium atoms³² as well as one trivalent lanthanide³³ per C_{60} cluster have been observed in the gas phase by mass spectrometry suggesting that C_n^{x-} ($x \leq 3$) anions exist in the gas phase. The distribution of electrons in the anionic clusters remains to be determined.³⁴

Conclusions

The discovery by Krätschmer et al.^{1,2} of a technique to produce and separate macroscopic quantities of the all carbon C_{60} molecule was a required first step in opening the door for exploring the molecular and bulk properties of this novel species. It is likely that C_{60} and C_{70} (as well as other C_n) pure carbon molecules and their associated derivatives shortly will be available in substantial quantity, opening the way to exploiting these materials in such diverse areas as organic chemistry, lubrication, materials science, solid-state physics, energy storage, polymer science, and catalysis.

Acknowledgment. We acknowledge the technical assistance of G. J. Dechert in obtaining mass spectral data. We thank the following people for providing preprints prior to publication, Prof. Richard Smalley, Prof. Robert Whetten, and Dr. Donald Bethune.

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(34) Magnetic resonance techniques are currently employed to examine the reduced carbon clusters.

Synthesis of [(mes)OsH(CH₃)CO] from [(mes)OsCl₂]_n and C₂H₅OH. Controlled Fragmentation of Ethanol into CH₃, H, CO, and H₂ by a Transition-Metal Center

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Abstract: In contrast to the reaction of [(mes)OsCl₂]_n (1: mes = mesitylene, 1,3,5-trimethylbenzene) with Na₂CO₃/EtOH under an ethylene atmosphere which gives [(mes)Os(C₂H₄)₂] (3), the corresponding reaction in the presence of propene leads to the formation of [(mes)OsH(CH₃)CO] (2) and [(mes)Os(η³-C₃H₅)Cl] (4) in about equal quantities. If H₂C=CH-*t*-Bu is used instead of propene, only 2 is obtained. In the absence of olefin, the reaction of 1 with Na₂CO₃/EtOH gives [(mes)₂Os₂(μ-OEt)₃]Cl (5). Experiments done in C₂D₅OD (leading to 2-*d*₄) and with propene in propan-2-ol (leading only to 4) provide evidence that all three ligands H, CH₃, and CO coordinated to the metal center in 2 are generated from C₂H₅OH. This is the first example illustrating that a controlled fragmentation of a primary alcohol into an alkyl group, CO, H, and H₂ can occur, the added olefin being the trap of H₂.

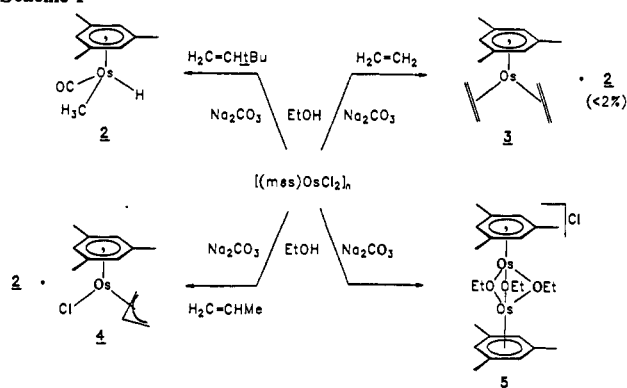
Introduction

Hydrido-transition-metal complexes are usually prepared from halogeno metal derivatives and compounds such as NaBH₄, LiAlH₄, or Na[AlH₂(OC₂H₄OMe)₂] (red-al) as the hydride source.¹ There are, however, also reports in the literature^{2,3} that

hydrido as well as carbonyl hydrido complexes can be obtained more simply on treatment of chloro, bromo, or iodo metal com-

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Scheme I



pounds with primary or secondary alcohols. It has been assumed that the substrate molecule RCH_2OH is formally split into $\text{R}-\text{H}$, CO , H^+ , and H^- , the formation of carbon monoxide and of the alkane being the main driving force.^{2b,c} Later, aldehydes have also been detected as byproducts in these fragmentation reactions.⁴ As far as we know there was no evidence up to now that a *hydrido*, a *carbonyl*, and an *alkyl group generated from the same alcohol molecule* can be trapped on the reactive metal center.

In continuation of our work on arene-osmium(II) and -osmium(0) complexes as potential starting materials for C-H activation processes,⁵⁻⁸ we have investigated in some detail the reactivity of the compound $[(\text{mes})\text{OsCl}_2]_n$ (**1**)^{9,10} toward terminal alkenes in alcohol solvents. In this paper, we describe the direct synthesis of $[(\text{mes})\text{OsH}(\text{CH}_3)\text{CO}]$ (**2**) from **1** and ethanol in the presence of 3,3-dimethyl-1-butene and the identification of a new allyl osmium complex formed as a second product if propene is used as the olefinic substrate. We note that compounds of the general type $[\text{L}_n\text{MH}(\text{CH}_3)\text{CO}]$ have been postulated as crucial intermediates in the catalytic production of H_2 from $\text{C}_2\text{H}_5\text{OH}$ and are assumed to rapidly decompose by CH_4 or CO elimination.¹¹

Results

The bis(ethylene)-osmium complex $[(\text{mes})\text{Os}(\text{C}_2\text{H}_4)_2]$ (**3**) has recently been prepared from **1** and $\text{Na}_2\text{CO}_3/\text{EtOH}$ under an ethylene atmosphere,⁹ in close analogy to the synthetic procedure reported by Bennett et al. for $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{C}_2\text{H}_4)_2]$.¹² Depending on the reaction conditions, occasionally small amounts of a by-product are formed which can be separated from **3** by treatment with CCl_4 and subsequent sublimation in vacuo. Although owing to the low yield the compound could not be characterized by elemental analysis, it was unambiguously shown by IR measurements to be **2**. This hydrido methyl complex is the photo-product both from $[(\text{mes})\text{OsH}_2(\text{CO})]$ and $[(\text{mes})\text{Os}(\text{CO})_2]$ in CH_4 matrices⁸ and has originally been synthesized from $[(\text{mes})\text{OsCH}_3(\text{CO})\text{I}]$ and Na/Hg in THF/EtOH .⁹ Complex **2** is

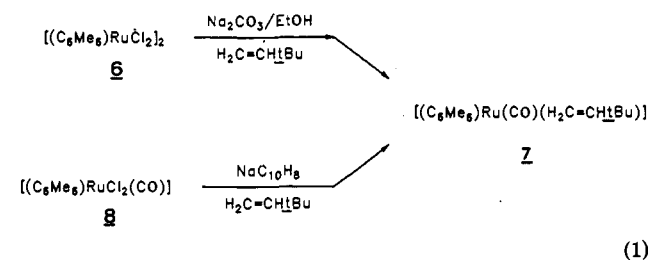
structurally related to the iridium compound $[(\text{C}_5\text{Me}_5)\text{IrH}(\text{CH}_3)\text{CO}]$ which is obtained on photolysis of $[(\text{C}_5\text{Me}_5)\text{Ir}(\text{CO})_2]$ in the presence of methane.¹³

The reaction of **1** with propene in the presence of $\text{Na}_2\text{CO}_3/\text{EtOH}$ gives two products which are separated by column chromatography. They have been identified as **2** and $[(\text{mes})\text{Os}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]$ (**4**) (Scheme I). The analogous allyl-benzene complex $[(\text{C}_6\text{H}_6)\text{Os}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]$ is known and has been prepared from $[(\text{C}_6\text{H}_6)\text{OsCl}_2]_2$ and $\text{C}_3\text{H}_5\text{HgCl}$ in 52% yield.¹⁴

If 3,3-dimethyl-1-butene, which has no allylic hydrogens, is used instead of propene, the formation of an allyl complex is excluded and only **2** is obtained. Coordination of the alkene or a derivative derived therefrom is not observed in this case. Nevertheless, the olefin plays a dominant role in this reaction as in the absence of $\text{H}_2\text{C}=\text{CH}-t\text{Bu}$ the dinuclear ethoxide-bridged cation $[(\text{mes})_2\text{Os}_2(\mu\text{-OEt})_3]^+$ is formed. It has been isolated and analytically characterized as the chloride salt **5**. We note that a similar compound $[(p\text{-cym})_2\text{Os}_2(\mu\text{-OMe})_3]\text{PF}_6$ ($p\text{-cym} = 1,4\text{-MeC}_6\text{H}_4\text{-}i\text{-Pr}$) is already known and has been prepared from $[(p\text{-cym})\text{Os}(\text{OAc})_2]$ and MeOH/KPF_6 .¹⁵

The reaction of **1** with propene in *propan-2-ol* exclusively gives the allyl complex **4**. This finding illustrates that in the reactions summarized in Scheme I ethanol behaves not only as the solvent but, more importantly, also as a *substrate*. The obvious conclusion that *all the ligands* coordinated to the metal center in **2** are generated from $\text{C}_2\text{H}_5\text{OH}$ is strongly supported by the result that in $\text{C}_2\text{D}_5\text{OD}$ besides **4** only the deuterated compound $[(\text{mes})\text{OsD}(\text{CD}_3)\text{CO}]$ (**2-d₄**) is formed. It has been proved by a separate experiment that **2-d₄** does not incorporate H from $\text{C}_2\text{H}_5\text{OH}$, if it is heated for 2 h under reflux. The finding that the reaction of **1** with 3,3-dimethyl-1-butene in ethanol to give **2** can also be done with NaOH as the base confirms that Na_2CO_3 is not the source of the CO ligand.

The arene-ruthenium complex $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ (**6**), which in the presence of CO and phosphines behaves similarly as **1**,¹⁶ does not react with 3,3-dimethyl-1-butene and Na_2CO_3 in ethanol to give $[(\text{C}_6\text{Me}_6)\text{RuH}(\text{CH}_3)\text{CO}]$. The only product extracted from the reaction mixture is the ruthenium(0) compound $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{CO})(\text{H}_2\text{C}=\text{CH}-t\text{Bu})]$ (**7**), which can also be obtained by reduction of $[(\text{C}_6\text{Me}_6)\text{RuCl}_2(\text{CO})]$ (**8**) with $\text{NaC}_{10}\text{H}_8$ in the presence of $\text{H}_2\text{C}=\text{CH}-t\text{Bu}$. This route has already been used for the synthesis both of $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{CO})(\text{H}_2\text{C}=\text{CHR})]$ ($\text{R} = \text{H}, \text{Me}$) and the corresponding benzene-ethylene-osmium complex $[(\text{C}_6\text{H}_6)\text{Os}(\text{CO})(\text{C}_2\text{H}_4)]$.^{7a} In the reaction of **6** with $\text{Na}_2\text{CO}_3/\text{EtOH}$ the hydrido methyl compound $[(\text{C}_6\text{Me}_6)\text{RuH}(\text{CH}_3)\text{CO}]$ is possibly formed as an intermediate. It may lose



(1)

methane by reductive elimination to generate the 16-electron fragment $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{CO})]$ which is trapped by the olefin to give **7**. Complex **7** is a yellow air-sensitive solid which has been characterized by MS and ^1H NMR spectroscopy.

Discussion

The most important result emerging from our work on the reactivity of the arene-dichloro-osmium complex **1** toward olefins

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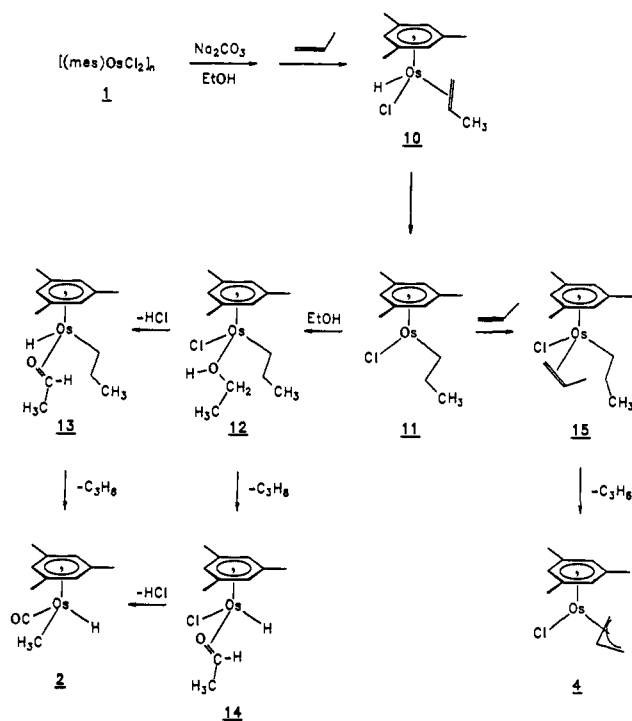
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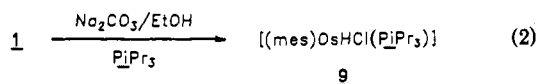
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Scheme II



in the presence of $\text{Na}_2\text{CO}_3/\text{EtOH}$ is that depending on the substituent R of the olefinic substrate $\text{H}_2\text{C}=\text{CHR}$ completely different types of products are obtained. The synthesis of ethylene- and η^3 -allyl-ruthenium complexes from $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ and ethylene or propene under similar conditions has already been reported,¹⁷ but there is no precedent for the formation of a carbonyl hydrido methyl compound from a related metal precursor.

In agreement with Bennett's results¹⁷ we feel that the course of the reactions summarized in Scheme I is best understood by considering a chloro hydrido complex as a primary intermediate. In the absence of olefin this labile intermediate assumed to be $[(\text{mes})\text{OsHCl}(\text{S})]$ (S = solvent) can be trapped by triisopropylphosphine to give the stable complex **9** in virtually quantitative yield (eq. 2). If $\text{C}_2\text{H}_5\text{OD}$ is used as the solvent, there



is no deuterium label found in the product **9**, in analogy with early work on the formation of metal hydrides from basic ethanol.¹⁸ Recently, the analogous benzene-osmium derivative $[(\text{C}_6\text{H}_6)\text{OsHCl}(\text{P}-i\text{Pr}_3)]$ has been prepared in our laboratory by treatment of $[(\text{C}_6\text{H}_6)\text{OsI}_2(\text{P}-i\text{Pr}_3)]$ with zinc dust in methanol.^{6b}

The mechanistic scheme for the reaction of **1** with propene which gives the two new mesitylene-osmium compounds **2** and **4** in about equal quantities is shown in Scheme II. We assume that a common intermediate **11** formed by olefin insertion into the Os-H bond of the chloro hydrido compound **10** is involved which owing to its coordinatively unsaturated behavior reacts either with ethanol or with propene to give the 18-electron species **12** or **15**, respectively. Elimination of propane and, in case of **12**, also of HCl leads to the formation of the final products. It is important to note that on both routes one olefin molecule behaves as a dihydrogen acceptor which is probably also true for the reactions of **1** with ethylene and 3,3-dimethyl-1-butene. In the reaction of **1** with $\text{Na}_2\text{CO}_3/\text{ethanol}$ and *tert*-butylethylene, 2,2-dimethylbutane was identified as a byproduct by GC measurements. As treatment of **1** with Na_2CO_3 and $\text{CH}_2=\text{CH}-t\text{-Bu}$ in $\text{C}_2\text{H}_5\text{OD}$ also gives $[(\text{mes})\text{OsH}(\text{CH}_3)\text{CO}]$ (**2**), the hydride ligand

must originate from the CH_2 group of the alcohol. A complete isotopic labeling study of this complex reaction which will include substituted *tert*-butylethylenes as substrates is in progress.

The final conclusion from the work presented in this paper is that on interaction with a reactive transition-metal center a complete and controlled fragmentation of a primary alcohol such as $\text{C}_2\text{H}_5\text{OH}$ into an alkyl group, CO, H, and H_2 can occur. It probably depends on the metal and the coordination sphere which of these species remain bonded to the metal center. Further studies should be aimed to find an efficient catalyst for the formation of RH, CO, and H_2 from RCH_2OH which in the case of ethanol is thermodynamically favored at room temperature.¹¹ We believe that compounds such as $[(\text{C}_n\text{R}_n)\text{MX}_2]_m$ might be good candidates for this purpose and are now testing this hypothesis.

Experimental Section

General Considerations. All manipulations were conducted under argon with rigorous exclusion of air. Solvents were dried by known procedures and distilled under argon prior to use. The starting materials **1**, **6**, and **8** were prepared by published methods.^{9,10,12,16} Triisopropylphosphine was a commercial product from Strem.

Reaction of 1 with Propene. (a) A suspension of **1** (105 mg, 0.14 mmol for $n = 2$) in 10 mL of ethanol was treated with excess Na_2CO_3 (ca. 200 mg) and under a continuous stream of propene warmed to 80 °C for 2 h. After the solution was cooled to room temperature, the solvent was removed in vacuo and the residue was extracted twice with 10 mL of benzene/hexane (1:1). The solution was concentrated to ca. 5 mL and then chromatographed on Al_2O_3 (neutral, activity grade III). With benzene/hexane (1:1) two fractions were eluted which contained the complexes **2** and **4** without any impurities.

Complex **2** (35 mg, 36%) was identified by comparison of the IR and ^1H NMR spectroscopic data with those recently reported.⁹ Complex **4** was obtained as a yellow microcrystalline solid; yield 40 mg (38%). ^1H NMR (C_6D_6 , 25 °C, 90 MHz) δ 4.48 (s, 3 H, $\text{C}_6\text{H}_3\text{Me}_3$), 4.35 (m, 1 H), 3.31 (d, br, $J_{\text{HH}} = 6.5$ Hz, 2 H), 3.03 (d, br, $J_{\text{HH}} = 9.9$ Hz, 1.62 (s, 9 H, $\text{C}_6\text{H}_3\text{Me}_3$). ^{13}C NMR (C_6D_6 , 25 °C, 50.3 MHz) δ 92.6 (s, CCH_3), 76.5 (s, CH of mes), 18.1 (s, CH_3), 76.0 (s, CH of allyl), 46.0 (s, CH_2). MS (70 eV) m/z 388 (50, M^+), 347 (100, $\text{M}^+ - \text{C}_3\text{H}_5$). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{ClOs}$: C, 37.25; H, 4.43. Found: C, 36.97; H, 4.27.

If ethanol- d_6 was used as the solvent, besides **4** the compound $[(\text{mes})\text{OsD}(\text{CD}_3)\text{CO}]$ (**2-d₄**) was obtained. It was characterized by MS (m/z 360; M^+) and NMR spectroscopic data.

(b) The reaction was analogous to that described for (a) but with propan-2-ol as the solvent. In this case, only complex **4** was obtained; yield 49%.

Reaction of 1 with 3,3-Dimethyl-1-butene. (a) The reaction was analogous to that described for the reaction with propene using 0.5 mL of $\text{H}_2\text{C}=\text{CH}-t\text{-Bu}$. The crude product was purified by sublimation in vacuo (40 °C, 10^{-4} mbar); yield of complex **2** 41%.

(b) The reaction was analogous to that described for (a) but using NaOH as the base; yield 56%.

(c) The reaction was analogous to that described for (a). After the reaction mixture was cooled to room temperature the volatiles were evaporated and condensed in a N_2 -cooled trap. This mixture was analyzed by GC (Varian aerograph; column 3% SE30, $20 \times 3/4$ in.; carrier gas He) and shown to contain 2,2-dimethylbutane besides 3,3-dimethyl-1-butene.

Preparation of $[(\text{mes})_2\text{Os}_2(\mu\text{-OEt})_3]\text{Cl}$ (5**).** The reaction was analogous to that described above but *without* the presence of an olefin. After the solvent was removed in vacuo, the residue was extracted with CH_2Cl_2 . The crude product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to give colorless crystals; yield 72 mg (66%). ^1H NMR (CD_2Cl_2 , 25 °C, 90 MHz) δ 5.59 (s, 6 H, $\text{C}_6\text{H}_3\text{Me}_3$), 4.57 (q, $J_{\text{HH}} = 6.8$ Hz, 6 H, OCH_2CH_3), 2.29 (s, 18 H, $\text{C}_6\text{H}_3\text{Me}_3$), 1.27 (t, $J_{\text{HH}} = 6.8$ Hz, 9 H, OCH_2CH_3). Anal. Calcd for $\text{C}_{24}\text{H}_{39}\text{ClO}_5\text{Os}_2$: C, 36.42; H, 4.97. Found: C, 35.94; H, 4.67.

Preparation of $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{CO})(\text{H}_2\text{C}=\text{CH}-t\text{-Bu})]$ (7**).** (a) The reaction was analogous to that described for the reaction of **1** with 3,3-dimethyl-1-butene but at 60 °C; yield ca. 10–15%. IR (hexane) $\nu(\text{CO})$ 1895 cm^{-1} . ^1H NMR (C_6D_6 , 25 °C, 200 MHz) δ 2.12 (dd, $J_{\text{HH}} = 11.2$ and 1.0 Hz, 1 H), 1.81 (dd, $J_{\text{HH}} = 11.2$ and 8.2 Hz, 1 H), 1.79 (s, 18 H, C_6Me_6), 1.40 (dd, $J_{\text{HH}} = 8.2$ and 1.0 Hz, 1 H), 1.22 (s, 9 H, *t*-Bu). MS (70 eV) m/z 376 (16, M^+), 292 (42, $\text{M}^+ - \text{H}_2\text{C}=\text{CH}-t\text{-Bu}$), 264 (100, $\text{C}_6\text{Me}_6\text{Ru}^+$). (b) The reaction was analogous to that described for the reaction of **8** with ethylene and propene;^{7a} yield ca. 20%.

Preparation of $[(\text{mes})\text{OsHCl}(\text{P}-i\text{Pr}_3)]$ (9**).** (a) A suspension of **1** (105 mg, 0.14 mmol for $n = 2$) in 10 mL of ethanol was treated with excess Na_2CO_3 (ca. 200 mg) and 0.15 mL of *P*-*i*-Pr₃ and warmed to 80 °C for 2 h. After the mixture was cooled to room temperature, the solvent was removed in vacuo, the residue extracted with benzene, and the concn-

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trated solution chromatographed on Al₂O₃ (neutral, activity grade III). With benzene, an orange-yellow fraction was eluted from which a yellow microcrystalline solid was obtained; yield 113 mg (81%). IR (KBr) $\nu(\text{OsH})$ 2050 cm⁻¹. ¹H NMR (C₆D₆, 25 °C, 200 MHz) δ 4.70 (s, 3 H, C₆H₃Me₃), 2.37 (d of sept, $J_{\text{HH}} = 7.2$, $J_{\text{PH}} = 10.0$ Hz, 3 H, PCHCH₃), 2.08 (s, 9 H, C₆H₃Me₃), 1.20 (dd, $J_{\text{HH}} = 7.2$, $J_{\text{PH}} = 12.9$ Hz, 9 H, PCHCH₃), 1.09 (dd, $J_{\text{HH}} = 7.2$, $J_{\text{PH}} = 12.9$ Hz, 9 H, PCHCH₃), -8.92 (d, $J_{\text{PH}} = 44$ Hz, OsH). ³¹P NMR (C₆D₆, 25 °C, 36.2 MHz) δ 22.6 (s). Anal. Calcd for C₁₈H₃₄ClO₅P: C, 42.63; H, 6.76; M_r, 507.1. Found: C, 42.40; H, 6.98; M_r, 508 (MS). (b) The reaction was analogous to that

described for (a) but with EtOD as the solvent. Yield of complex **9** 80%.

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Photooxidation of the Molybdenum and Tungsten Carbynes ($\eta^5\text{-C}_5\text{H}_5$)L₂M≡CR [L = P(OMe)₃, CO and R = Ph, Me, c-C₃H₅]

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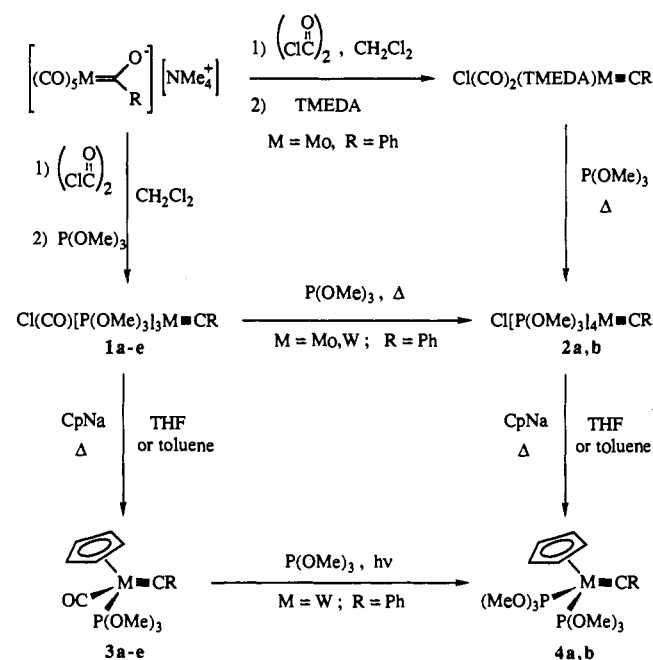
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Abstract: Photolysis of the carbyne complexes CpL₁L₂M≡CR, **3a-d** and **4a,b** (M = Mo, W; L₁ = P(OMe)₃; L₂ = CO, P(OMe)₃; R = Ph, Me, c-C₃H₅), in chlorinated solvents in the presence of PMe₃ results in the formation of the cationic complexes [Cp(Cl)(PMe₃)₂M≡CR]⁺Cl⁻ (**5a-d**). All of the carbyne complexes were spectroscopically characterized. The formation of **5a-d** is postulated to involve electron transfer from the MLCT excited states of the carbynes to the chlorinated solvent. The resulting 17e⁻ species then undergo ligand exchange followed by halogen atom abstraction to afford the observed cationic complexes. UV-visible spectroscopy of **3a-d** and **4a,b** has established that electron transfer occurs upon MLCT excitation rather than from CTTS transitions, while EHMO calculations on the model system Cp[P(OH)₃]₂Mo≡CPh are in agreement with the MLCT band being d - π* in nature. For the cases L₁ = P(OMe)₃, L₂ = CO, R = Ph or tolyl, the MLCT state was also responsible for emission in fluid solution at room temperature. The carbyne Cp(CO)[P(OMe)₃]W≡C(o-Tol) (**3e**) was characterized by X-ray crystallography: monoclinic, C2/c, a = 32.754 (10) Å, b = 7.294 (3) Å, c = 15.521 (7) Å, β = 98.982 (5)°, V = 3662.5 (5) Å³, Z = 8, R(F) = 5.0%, R(wF) = 5.6% for 1692 reflections, F_o ≥ 3σ(F_o).

Introduction

Although the photochemistry of organometallic compounds generally leads to ligand loss as the primary photoprocess,¹ photolysis of metal-carbyne complexes has recently been shown to lead to several interesting reaction types. The carbyne Cp(CO)₂W≡CTol undergoes intramolecular coupling of the carbyne ligand to a carbonyl.² The resulting coordinatively unsaturated η²-ketenyl complex can be trapped with PPh₃. Similar photochemical coupling reactions have been postulated to occur in Br(PMe₃)₂(CO)₂W≡CPh³ and Tp'(CO)₂Mo≡CPh.⁴ There are reports of photochemical addition of HCl to the metal-carbon triple bonds of both the neutral and cationic osmium phenyl carbynes, Os(CPh)(CO)Cl(PPh₃)₂ and [Os(CPh)(CO)₂(PPh₃)₂]⁺.⁵ The unusual photochemical rearrangement of (Cp)[P(OMe)₃]₂Mo≡CCH(^tBu)CO^tBu results in a π-allyl complex, suggesting insertion of the carbyne carbon into a C-H bond.⁶ Photolysis of the related neopentyl carbyne, (Cp)[P(OMe)₃]₂Mo≡CCH₂^tBu, in the presence of diphenylacetylene was reported to produce an η³-cyclopropenyl complex.⁷ All of

Scheme I



these modes of reactivity have been attributed to the presence of low-lying metal-to-ligand charge-transfer (MLCT) excited states, from which reaction occurs.

We recently reported an additional class of reaction for excited state metal carbynes in which photooxidation produces highly

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