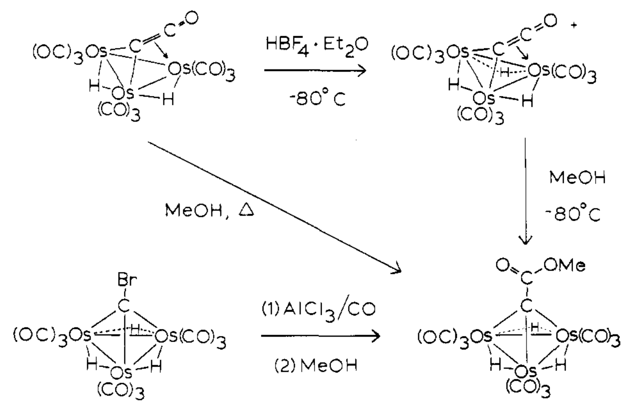
Scheme I



Under the same conditions ($CDCl_3$, 25 °C) the osmium carbonyl carbons appear as broad resonances at δ 165.8 and 175.6 (ratio 2:1). However, at a lower temperature a 2:2:1:2:2 pattern is observed (−60 °C, CD_2Cl_2, δ 179.6, 173.0, 169.9, 168.0, 158.3). If the hydride ligands in $H_2Os_3(CO)_9(CCO)$ are placed unsymmetrically as shown in IV, which is proposed in analogy with the arrangement established for $H_2Os_3(CO)_9(CCH_2)$ (V),[4] then the low-temperature ^1H and ^{13}C NMR data require rapid hydride equilibration. Alternatively, the actual hydride positions in $H_2Os_3(CO)_9(CCO)$ may be equivalent.

The reactivity of $H_2Os_3(CO)_9(CCO)$ is consistent with its formulation (see Scheme I). Heating the ketenylidene complex in methanol affords the carbomethoxymethylidyne cluster, $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$. The same alkylidyne cluster may be prepared from $H_2Os_3(CO)_9(CCO)$ by an alternative procedure. Treatment of a CH_2Cl_2 solution of $H_2Os_3(CO)_9(CCO)$ with $HBF_4 \cdot OEt_2$ at −80 °C gives an off-white precipitate (presumably $[H_3Os_3(CO)_9(CCO)]^+$ or $[H_2Os_3(CO)_9(CCOH)]^+$) which reacts with methanol at −80 °C to afford $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$ (mass spectrum, m/z 902 M^+ (^{192}Os); ^1H NMR ($CDCl_3$, 35 °C) τ 6.17 (s, 3 H), 29.38 (s, 3 H); IR (ν(CO), C_6H_{12}) 2116 vw, 2089 vs, 2081 w, sh, 2030 ms, 2025 vs, 2015 mw, 1688 vw) in high yield. $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$ can also be prepared by treating $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$[5] with $AlCl_3$ in CH_2Cl_2 under CO followed by addition of methanol. An analogous procedure was used by Seyferth to prepare $Co_3(CO)_9(\mu_3\text{-}CCO_2Me)$[6] and by Keister to prepare $H_3Ru_3(CO)_9(\mu_3\text{-}CCO_2Me)$.[5]

The sequence of C–H bond cleavage and C–C bond formation in the conversion of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ to $H_2Os_3(CO)_9(CCO)$ is not yet clear. Possible intermediates include IIIa or IIIb, II, or a complex of ketene. Transfer of an alkylidene ligand to coordinated CO is known in mononuclear transition-metal chemistry.[7] Transfer of CO to alkylidyne ligands has also been observed.[8] The migration of coordinated CO to a carbon center has been proposed to account for the formation of $[Co_3(CO)_9CCO]^+$ from $Co_3(CO)_9(\mu_3\text{-}CCl)$ and $AlCl_3$[6] and for the formation of $[Fe_4(CO)_{12}(\mu_4\text{-}CCO_2Me)]^-$ from the oxidation of $[Fe_6C(CO)_{16}]^{2+}$ by tropylium bromide in methanol.[9,10]

Acknowledgment. This research has been supported at the University of Illinois by National Science Foundation Grants DMR 80-20250 and CHE 81-00140. Support of this research at The Pennsylvania State University has been provided by the Department of Energy, Office of Basic Energy Sciences. J.R.S. and G.L.G. acknowledge the Alfred P. Sloan Foundation for research fellowships and the Camille and Henry Dreyfus Foundation for Teacher–Scholar awards.

Registry No. I, 77208-32-3; IV, 78697-97-9; $[Os_3(CO)_{11}CHO]^-$, 73788-03-1; $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$, 78697-98-0; $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$, 73746-96-0.

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Preparation of Dianionic Carbonyl Complexes of Molybdenum and Tungsten

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Summary: Reduction of $[M(CO)_5(NMe_3)]$ (M = Cr, Mo, W) in THF with alkali naphthalides gives high purity solutions of the corresponding $[M(CO)_5]^{2-}$ dianions. Stable crystalline salts of the $[M(CO)_5]^{2-}$ dianions (M = Mo, W) were prepared by complexing the sodium counterions with a cryptand. Reduction of $[W(CO)_4(NH_3)\{P(i\text{-}Pr)_3\}]$ with sodium naphthalide gives $[W(CO)_4\{P(i\text{-}Pr)_3\}]^{2-}$, as demonstrated by reaction with Ph_3SnCl and counterion exchange to give $[NEt_4][W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$.

The development of the chemistry of the pentacarbonyl dianions of molybdenum and tungsten has been severely restricted by the lack of a convenient preparation of solutions of the complexes in an innocuous solvent such as an ether.[1] We wish to report new syntheses of these dianions using an alkali naphthalide as the reductant[8] which provide direct excess to high purity solutions of the

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(1) As noted by others,[2] Behrens' procedures are technically difficult and only suitable for preparing small quantities of the dianions[3,4] or give samples contaminated with other salts.[5] The cesium salts $Cs_2[M(CO)_5]$ (M = Cr, Mo, W), prepared by Cs/Hg reduction of the corresponding hexacarbonyls, are insoluble in ethereal solvents and are usually contaminated with Hg.[6] In our hands, the reduction of $[W(CO)_6]$ with Na/Ng in dimethoxyethane[7] invariably resulted in mixtures of $Na_2[W_2(CO)_{10}]$ and $Na_2[W(CO)_5]$, an observation which is consistent with the published spectra of such reactions and with the rather low yields reported for some of the reactions carried out by using material prepared in this way.[7] Only reduction of the hexacarbonyls with Na in hexamethylphosphoramide[2] gives pure samples of the dianions in a convenient reaction, but the reactivity and high boiling point of this solvent considerably restrict the utility of this approach.[6]

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complexes in tetrahydrofuran (THF) and from which we have been able to obtain stable crystalline salts of both dianions. Alkali naphthalide reduction has also been applied to the preparation of $[W(CO)_4\{P(i\text{-}Pr)_3\}]^{2-}$, the first phosphine-substituted derivative of $[W(CO)_5]^{2-}$. The new syntheses will for the first time allow a thorough exploration of the chemistry of the dianions; recent results from our laboratories on their reactions with iminium salts[9] and CO_2,[10] together with Collman's work on the isoelectronic complex $Na_2[Fe(CO)_4]$[11] and Ellis' earlier work on the group 6A carbonyl dianions themselves[2,6,7] would suggest that this is likely to be extensive.

The reactions involve electron transfer from an alkali naphthalide to a carbonyl complex containing a labile donor ligand[12] (eq 1). For example, $Na_2[W(CO)_5]$ is

$$[M(CO)_5L] \xrightarrow[-L]{2M'C_{10}H_8} M'_2[M(CO)_5] \qquad (1)$$

$$M = W,\ M' = Li,\ Na \qquad M = Mo,\ M' = Na$$

prepared by syringing a 0.2M THF solution of $NaC_{10}H_8$ dropwise into a 0.1 M THF solution of $[W(CO)_5(NMe_3)]$[13] at −78 °C until the orange solution begins to change color sharply to a dark red-orange.[14] After the mixture is warmed to room temperature, IR spectra of the solution, which is now homogeneous and orange, typically show the presence of $[W(CO)_5]^{2-}$[15] with only trace amounts of $[W_2(CO)_{10}]^{2-}$[16] as a contaminant. The dianion was identified chemically by its reaction with Ph_3SnCl,[6] which gave, after counterion exchange and recrystallization, a 65% yield[17] of $[NEt_4][W(CO)_5SnPh_3]$.[18] Naphthalene free solutions of the dianion are readily prepared on a millimole scale by removing all but a few milliliters of the solvent from a solution of the dianion under vacuum at 0 °C and washing the residue with diethyl ether at 0 °C to give an orange solid which can be redissolved in THF. The solid salt is unstable above 0 °C, and a significant quantity of the material will not redissolve in THF after 15 min at 25 °C.[19] Solutions of the dianion are extremely air sensitive but are stable at room temperature under N_2 for several days.

The tungsten dianion can also be prepared by $NaC_{10}H_8$ reduction of a suspension of $[W(CO)_6]$ in THF at −78 °C, but the very limited solubility of the hexacarbonyl necessitates very careful addition of the reductant, and it is more convenient to use the soluble amine as the substrate.

An analogous reaction of $NaC_{10}H_8$ with $[Mo(CO)_5(NMe_3)]$[20] gives solutions of $Na_2[Mo(CO)_5]$ in THF. The only difference between this and the tungsten case is that the solid salt is less thermally stable, and the solvent must be removed at −30 °C and the solid washed at −30 °C when preparing naphthalene free solutions. The dianion was identified by solution IR spectroscopy[21] and further characterized chemically by its reaction with Ph_3SnCl[6] to give, after counterion exchange and recrystallization, a 90% yield of $[Mo(CO)_5SnPh_3][NEt_4]$.[18] The complex $Na_2[Cr(CO)_5]$[6] can be prepared in a similar manner.

The tungsten dianion was also prepared as the lithium salt, using $LiC_{10}H_8$ as the reductant. This salt is chemically identical to the sodium salt but has a markedly different IR spectrum in THF solution.[22] Since the available data on the solution ion pairing of $Na_2[Fe(CO)_4]$[23] would suggest that both the sodium and lithium salts of the tungsten dianion are likely to be ion paired in THF, these features suggest a qualitatively different interaction between the different cations and the dianions. The most reasonable explanation is that the Li^+ cations undergo a strong isocarbonyl interaction[24] with the oxygens of the carbonyl ligands.

Crystalline salts of both dianions were precipitated from THF solutions of the sodium salts by addition of 2 equiv of a cryptand,[25] Kryptofix 2:2:1,[26] to complex the sodium ions. The orange solids were recrystallized from dimethylformamide/THF, and IR spectra of Nujol mulls indicated that they contained $[W(CO)_5]^{2-}$ and $[Mo(CO)_5]^{2-}$, respectively.[27] Analyses were consistent with the anticipated formulas.[28] In marked contrast to solid samples of the sodium salt, crystalline samples of the $[Na(crypt)]^+$ salts appear to be stable indefinitely at room temperature. Cryptands have been used previously to prevent solution and solid-state interactions between an alkali-metal cation and a metal carbonyl anion,[29] but this is the first case in which elimination of this interaction has been reported to have a stabilizing effect on such salts.

The versatility of alkali naphthalide reduction as a route to transition-metal dianions was further demonstrated by the preparation of thermally unstable solutions of $[W(CO)_4\{P(i\text{-}Pr)_3\}]^{2-}$, the first phosphine-substituted derivative of $[W(CO)_5]^{2-}$. A 0.2 M solution of $NaC_{10}H_8$ in THF was slowly added to a 0.1 M solution of $[W(CO)_4\{P(i\text{-}Pr)_3\}(NH_3)]$[30] in THF at −78 °C until the orange solution began to darken sharply in color. The formation of $[W(CO)_4\{P(i\text{-}Pr)_3\}]^{2-}$ under these conditions is suggested by

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(14) This normally requires 2.0 equiv of $NaC_{10}H_8$, but this number is highly dependent on the purity of the $NaC_{10}H_8$. Less than 1% of free base, as measured by quenching with $BrCH_2CH_2Br$ followed by titration with 0.1 M aqueous HCl, will catalyze the consumption of additional naphthalide in side reactions.

(15) 1829 (vs), 1772 (s br) cm^{-1} (cf. lit.[6] 1827 (s), 1757 (s br) cm^{-1}).

(16) The principal absorption of $[W_2(CO)_{10}]^{2-}$ at 1890 cm^{-1} provides a sensitive probe for the presence of the dimeric species, which is the first oxidation product of $[W(CO)_5]^{2-}$, as well as a side product in some preparations.

(17) Yield based on the quantity of amine complex used in the reduction.

(18) Identified by comparison of the IR spectrum of the compound with that in the literature.[6] The ^1H NMR spectra of the compound in acetone-d_6 was also consistent with this formulation.

(19) The thermal instability of solid $Na_2[W(CO)_5]$ prepared in this manner is in marked contrast with the apparent stability of the materials for which Behrens reports analytical data.[4] In the absence of spectroscopic data for Behrens' compound, we are unable to resolve this conflict.

(20) $[Mo(CO)_5(NMe_3)]$ was conveniently prepared in 4-g quantities in 60–70% yield by treating 5 g of $[Mo(CO)_6]$ in 150 mL of THF with 1.5 equiv of Me_3NO in the presence of 20 equiv of Me_3N. We did not find a photochemical procedure to be a satisfactory route to this complex, a result consistent with the 46% yield reported previously.[13]

(21) 1828 (vs), 1768 (s br) cm^{-1} (cf. lit.[6] 1822 (s), 1757 (s br) cm^{-1}).

(22) $Li_2[W(CO)_5]$: 1820 (vs), 1775 (s, sh), 1690 (s), 1608 (s) cm^{-1} (cf. ref 15).

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(26) Kryptofix 2:2:1 is a proprietary name for 4,7,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, as purchased from Parish Chemical Co.

(27) $[Na(2:2:1)]_2[W(CO)_5]$: 1772 (s), 1725 (s) cm^{-1}. $[Na(2:2:1)]_2[Mo(CO)_5]$: 1772 (s), 1720 (s br) cm^{-1}.

(28) Anal. Calcd for $C_{37}H_{64}N_4Na_2O_{15}W$: C, 42.94; H, 6.23. Found: C, 43.08; H, 6.70. Anal. Calcd for $C_{37}H_{64}MoN_4Na_2O_{15}$: C, 46.94; H, 6.81. Found: C, 46.89; H, 6.78.

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the subsequent reaction of this solution with 1 equiv of Ph_3SnCl in THF at -78 °C to give a 57% yield of off-white needles of $Li[W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]\cdot 2THF$[31] after precipitation with benzene and recrystallization from Et_2O. Counterion exchange using $[NEt_4]Br$ in ethanol gives $[NEt_4][W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$, which recrystallized as off-white needles of a CH_2Cl_2 solvate[32] from CH_2Cl_2.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Exxon Educational Foundation, and the National Science Foundation (Grants CHE 78-25699 and CHE 80-16162) for financial support.

Registry No. $Na_2[Cr(CO)_5]$, 51233-19-3; $Na_2[Mo(CO)_5]$, 57127-94-3; $Na_2[W(CO)_5]$, 57127-91-0; $Li_2[W(CO)_5]$, 75706-82-0; $NaC_{10}H_8$, 3481-12-7; $LiC_{10}H_8$, 7308-67-0; $[Mo(CO)_5(NMe_3)]$, 15152-84-8; $[W(CO)_5(NMe_3)]$, 15228-32-7; $[Mo(CO)_5SnPh_3][NEt_4]$, 55971-56-7; $[NEt_4][W(CO)_5SnPh_3]$, 55971-72-7; $[W(CO)_5][Na(crypt)]_2$, 79199-37-4; $[Mo(CO)_5][Na(crypt)]_2$, 79135-07-2; $[W(CO)_4\{P(i\text{-}Pr)_3\}(NH_3)]$, 79199-38-5; $[W(CO)_4\{P(i\text{-}Pr_3\}]^{2-}$, 79135-08-3; $Li[W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$, 79135-09-4; $[NEt_4][W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$, 79135-11-8; $W(CO)_6$, 14040-11-0.

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(31) IR: ν(CO) (THF) 1978 (s), 1858 (vs), 1823 (s) cm^{-1}. ^1H NMR $[(CD_3)_2CO]$ δ 8.62–8.37 (m, 6 H, m-H of Ph), 8.07–7.72 (m, 9 H, o- and p-H of Ph), 3.64 (m, 8 H, OCH_2CH_2), 1.79 (m, 8 H, OCH_2CH_2), 1.12 (dd, 18 H, J = 6.4 Hz, J_{H-P} = 12.8 Hz, $CH(CH_3)_2$), $CH(CH_3)_2$ obscured by solvent.

(32) Anal. Calcd for $C_{39}H_{56}NO_4PSnW\cdot 0.5CH_2Cl_2$: C, 48.46; H, 5.82. Found: C, 48.65; H, 6.12. IR: ν(CO) (CH_2Cl_2) 1975 (s), 1863 (vs), 1810 (s) cm^{-1}. ^1H NMR $[(CD_3)_2CO]$: δ 7.75–7.63 (m, 6 H, m-H of Ph), 7.17–7.01 (m, 9 H, o- and p-H of Ph), 5.58 (s, 1 H, $0.5CH_2Cl_2$); 3.32 (q, 8 H, J = 7.3 Hz, CH_2CH_3), 2.00 (septuplet, 3 H, J = 7.2 Hz, $CH(CH_3)_2$, partially obscured by solvent), 1.31 (t of t, 12 H, J = 7.3 Hz, J_{H-N} = 1.6 Hz, CH_2CH_3), 1.11 (d of d, 18 H, J = 7.2 Hz, J_{HP} = 12.5 Hz, $CH(CH_3)_2$).

Synthesis and Structure of $[Ru(C_3Ph_2)(PMe_3)_2(Cp)][PF_6]$, a Cationic Diphenylallenylidene Complex

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Summary: The electron-rich complex $[RuCl(PMe_3)_2(Cp)]$ reacts with the alkynol $Ph_2C(OH)(C\equiv CH)$ and NH_4PF_6 to produce the novel diphenylallenylidene complex $[Ru(\eta^1\text{-}C{=}C{=}CPh_2)(PMe_3)_2(Cp)][PF_6]$. An X-ray structural determination reveals a nearly linear metallacumulene chain with a short (1.884 (5) Å) ruthenium–carbon bond.

The chemistry of transition-metal alkylidene (carbene) complexes is now well established,[1] but only recently have unsaturated alkylidenes (vinylidene complexes, $M{=}C{=}CR_2$) been explored.[2] Still more rare are examples of the cumulogs[3] of alkylidene complexes, allenylidene complexes ($M{=}C{=}C{=}CR_2$).[4] A simple method for the preparation of cationic ruthenium allenylidene complexes is reported here, along with the structure of one of these complexes.

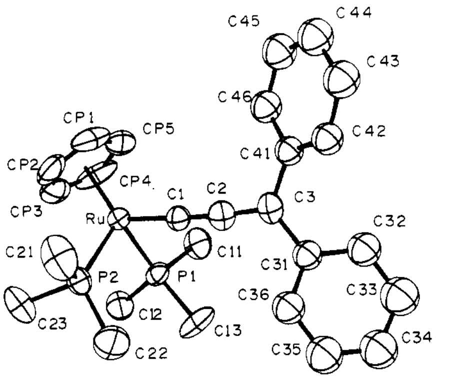

Figure 1. A perspective ORTEP diagram of the cation of $[Ru(C_3Ph_2)(PMe_3)_2(Cp)][PF_6]$ showing 50% probability ellipsoids.

Table I. Selected Bond Lengths and Angles with Errors for $[Ru(C_3Ph_2)(PMe_3)_2(CP)][PF_6]$

atoms	bond length, Å	atoms	angle, deg
Ru-C1	1.884 (5)	Ru-C1-C2	175.9 (5)
Ru-P1	2.289 (2)	C1-C2-C3	175.1 (7)
Ru-P2	2.292 (2)	C2-C3-C31	119.8 (6)
Ru-CPO[a]	1.929	C2-C3-C41	119.5 (6)
C1-C2	1.255 (8)	C31-C3-C41	120.7 (5)
C2-C3	1.329 (9)	P1-Ru-P2	94.57 (6)
C3-C31	1.462 (9)	P1-Ru-C1	87.0 (2)
C3-C41	1.511 (8)	P2-Ru-C1	92.4 (2)
		CPO[a]-Ru-C1	127.95

[a] CPO is the centroid of the cyclopentadienyl ring.

The reaction of $[RuCl(PMe_3)_2(Cp)]$[5] with the acetylenic alcohol $Ph_2C(OH)(C\equiv CH)$[6] and NH_4PF_6 in ethanol (25 °C, 27 h) leads to a deep orange-brown solution and a brown precipitate. Cooling, filtration, washing with water and ethanol, and drying in vacuo produces a 76% yield of a brown microcrystalline solid. Recrystallization from dichloromethane/ether yields large orange-brown crystals suitable for X-ray diffraction.

Spectroscopic characterization of the product suggests that is $[Ru(C_3Ph_2)(PMe_3)_2(Cp)][PF_6]$ (I), a cationic diphenylallenylidene complex. Strong infrared absorptions are found at 1926 and 840 cm^{-1} (in $CHCl_3$), corresponding to the asymmetric $C{=}C{=}C$ stretch of an allene system[7,8] and to the asymmetric stretch of the $[PF_6]^-$ ion,[9] respectively. The proton NMR spectra of several $[RuL(PMe_3)_2(Cp)]^+$ derivatives have suggested a direct relationship between the chemical shift of the cyclopentadienyl group and the degree of "electron richness" at the metal site.[5a] In light of this correlation, the ^1H NMR spectrum of complex I ($CDCl_3$, 90 MHz; δ 7.8–7.4 (m, Ph), 5.50 (s, Cp), 1.55 (br t, PMe_3)) suggests that the diphenyl-

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