compounds resulting from the reaction of a series of organometallic reagents with the α-H$_3$PW$_{11}$O$_{39}{}^{4-}$ anion and other polyoxoanions. Preliminary results indicate that the compound reported here is only the first representative of a large family of polyoxoanion supported organometallic compounds.

References and Notes

(1) Y. I. Yermakov, *Catal. Rev.—Sci. Eng.*, **13**, 77 (1976).
(2) D. G. H. Ballard, *Adv. Catal.*, **23**, 263 (1973).
(3) F. J. Karol, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem., Pap.*, **37**, 310 (1977).
(4) G. M. Brown, M. R. Noe-Spirlet, W. R. Busing, and H. A. Levy, *Acta Crystallogr., Sect. B*, **33**, 1038 (1977).
(5) T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).
(6) C. M. Tourné, G. F. Tourné, S. A. Malik, and T. J. R. Weakley, *J. Inorg. Nucl. Chem.*, **32**, 3875 (1970).
(7) P. T. Meiklejohn, M. T. Pope, and R. A. Prados, *J. Am. Chem. Soc.*, **96**, 6779 (1974).
(8) Crystal radii for coordination number six: R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).
(9) D. L. Kepert, "The Early Transition Metals", Academic Press, New York, 1972.
(10) P. C. Wailes, R. S. P. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium, and Hafnium", Academic Press, New York, 1974, pp 30–50.
(11) Calculated (found) weight percentages for C$_{69}$H$_{149}$N$_4$TiPW$_{11}$O$_{39}$: C, 22.04 (22.09); H, 3.99 (4.02); N, 1.49 (1.45); Ti, 1.27 (1.36); P, 0.82 (0.75); W, 53.78 (53.71).
(12) The Onsager limiting slope for 1 in CH$_3$CN is 2.6 × 10^3 Ω^{-1} cm^2 equiv$^{-3/2}$ L$^{1/2}$, a value which compares well with the slope of 2.5 × 10^3 Ω^{-1} cm^2 equiv$^{-3/2}$ L$^{1/2}$ for the 1:4 electrolyte α-[(n-C$_4$H$_9$)$_4$N]$_4$SiW$_{12}$O$_{40}$ in CH$_3$CN.
(13) The ^{1}H NMR spectrum of 1 in CD$_3$CN displays a C$_5$H$_5$ resonance at δ 6.5 ppm and an NCH$_2$ multiplet at δ 3.1–3.3 ppm with relative intensities 1: 6.6.
(14) C. Rocchiccioli-Deltcheff and R. Thouvenot, *J. Chem. Res. (M)*, 0549 (1977).
(15) Prepared by adding a solution of 1 in 1,2-C$_2$H$_4$Cl$_2$ to a mixture of CHCl$_3$ and saturated aqueous KI, and recrystallizing the resulting precipitate from H$_2$O.
(16) F. W. Siegert and H. J. de Liefde Meijer, *J. Organomet. Chem.*, **20**, 141 (1969).
(17) Pure 1 was recovered in >90% yield after addition of (n-C$_4$H$_9$)$_4$NBr to the aqueous solution.
(18) ^{17}O NMR chemical shifts have been demonstrated to be very sensitive to changes in metal–oxygen bond strengths: W. G. Klemperer and W. Shum, *J. Am. Chem. Soc.*, **99**, 3544 (1977); W. G. Klemperer and W. Shum, *ibid.*, **100**, 4891 (1978).
(19) A. Kobayashi and Y. Sasaki, *Bull Chem. Soc. Jpn.*, **48**, 885 (1975).
(20) Fellow of the Alfred P. Sloan Foundation, 1976–1978.

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Multiple Metal–Carbon Bonds. 12.[1] Tungsten and Molybdenum Neopentylidyne and Some Tungsten Neopentylidene Complexes

Sir:
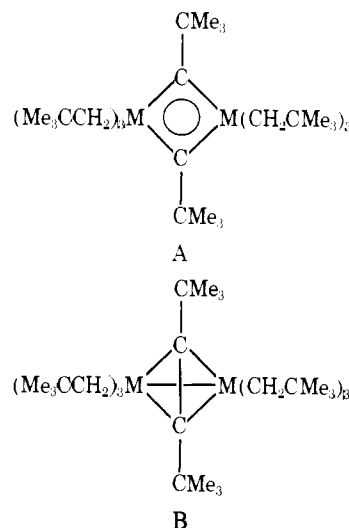
The formation of alkylidene ($=$CHR) and alkylidyne ($\equiv$CR) complexes of Nb and Ta by α-hydrogen abstraction, and acceleration of that process by adding small, basic tertiary phosphines, is now well established[1] (R = CMe$_3$ or C$_6$H$_5$). A significant question is whether any of these principles can be extended to group 4 or 6 metals. Establishing the latter is probably more important owing to the suspected role of W and Mo alkylidene complexes in the olefin metathesis reaction.[2] We present results here which demonstrate that this is possible. The rather extraordinary Mo and W complexes formed thereby are thermally stable, well-behaved, and easily characterized by standard techniques.

A clear, brilliant yellow solution is obtained when 6 mol of LiCH$_2$CMe$_3$ is added to WCl$_6$ in ether at -78 °C. When this

is warmed to 25 °C, the color darkens to red-brown. Removing the solvent in vacuo and subliming the residue at 70 °C (1 μ) gives yellow crystals of air-sensitive (Me$_3$CCH$_2$)$_3$W$\equiv$CCMe$_3$ (1) in 25% yield (eq 1) (Calcd for WC$_{20}$H$_{42}$: C, 51.51; H, 9.07. Found: C, 51.32; H, 8.90.). A similar reaction at 25 °C also gives 1 in 25% yield. The analogous -78 °C reaction between MoCl$_5$ and 5 mol of LiCH$_2$CMe$_3$ gives pale yellow, air- and light-sensitive (Me$_3$CCH$_2$)$_3$Mo$\equiv$CCMe$_3$ (2, 15% yield). Since the first mole of LiCH$_2$CMe$_3$ at 25 °C reduces W(VI) to W(V),[3] each reaction is not a straightforward double α abstraction (neopentyl $\rightarrow$ neopentylidene $\rightarrow$ neopentylidyne[1,4]) in a M(VI) alkyl complex. The tacky residue which remains after subliming out 1 or 2 gives broad, uninterpretable ^{1}H and ^{13}C NMR spectra. The residue is extremely soluble in pentane and no crystalline product could be obtained, even at -78 °C.

$$MCl_x + x\,LiCH_2CMe_3 \xrightarrow{\text{ether}} (Me_3CCH_2)_3M\equiv CCMe_3 \quad (1)$$

$$1, M = W; x = 6$$
$$2, M = Mo; x = 5$$
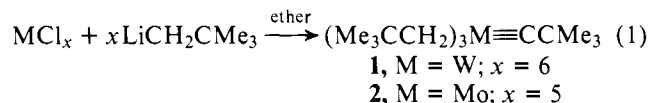
The molecular weight of 2 in cyclohexane is that expected for a dimer, while that of 1 is ~75% of that expected for the dimer.[5] The mass spectra of 1 and 2 show only the monomeric ion.[6] These data suggest that 1 and 2 are dimers which dissociate readily. (Further evidence for this behavior is the reaction of 1 with PMe$_3$ to give monomeric products.) The two most reasonable formulations, A and B, are based on known ex-

amples containing each type of MC$_2$M core. We favor A (or a distorted version thereof[7]) since two related molecules, [Nb(CH$_2$SiMe$_3$)$_2$(CSiMe$_3$)]$_2$[7b] and [W(CH$_2$SiMe$_3$)$_2$-(CSiMe$_3$)]$_2$[7c,8] are planar, since we have not been able to add acetylenes to (Me$_3$CCH$_2$)$_3$Mo$\equiv$Mo (CH$_2$CMe$_3$)$_3$[9] to give B-type molecules,[10,11] and since the ^{13}C signal for the bridging carbon in Mo$_2$Cp$_2$(CO)$_4$(MeC$\equiv$CMe) (a B-type molecule) is far upfield of where those in 1, 2, [W(CH$_2$SiMe$_3$)$_2$-(CSiMe$_3$)]$_2$, and [Ta(CH$_2$SiMe$_3$)$_2$(CSiMe$_3$)]$_2$ are found (see below).[12] The metal in known B-type molecules is also in a lower than maximum oxidation state, while that in known A-type molecules is in the maximum formal oxidation state.

The gated decoupled ^{13}C NMR spectrum of 1 in C$_6$D$_6$ shows only one set of six resonances.[13] Therefore, either monomer–dimer interconversion is fast on the ^{13}C NMR time scale or >~95% of one is present. The neopentylidyne C$_\alpha$ resonance is found at 317 ppm, at the high end of the range for C$_\alpha$ in terminal alkylidyne complexes of several types[4,14] and bridging alkylidyne α-carbon atoms in [W(CH$_2$SiMe$_3$)$_2$-(CSiMe$_3$)]$_2$ (353 ppm)[8b] and [Ta(CH$_2$SiMe$_3$)$_2$(CSiMe$_3$)]$_2$ (404 ppm).[8b] Its coupling to [183]W ($J_{CW} = 230 \pm 5$ Hz) is

slightly larger than in Fischer's carbyne complexes[14] and much larger than J_{CW} for the neopentyl C_α in **1** (89 Hz). (Note that neopentylidene C_α-W coupling constants are ~120 Hz (see below).) The relative size of the W satellites for the neopentylidyne C_α resonance is approximately the same as for the neopentyl C_α resonance, consistent with (but not proving[15]) a monomer ↔ dimer interconversion rapid enough to "decouple" the second W atom in the dimer. The ^{13}C NMR spectrum of **2** is analogous.[16]

$(Me_3CCH_2)_3W\equiv CCMe_3$ reacts rapidly (5 min) and quantitatively with neat PMe_3 in a sealed tube at 100 °C. (No further change occurs in 1 day.) One mole of neopentane evolves (GLC) and yellow crystals of **3** are left behind on removing PMe_3 in vacuo. **3** is soluble in pentane, crystallizes readily, and is a monomer in cyclohexane (calcd 546, found 530). The ^{13}C NMR spectrum of **3** in C_6D_6[17] shows a neopentyl ligand ($\delta(C_\alpha)$ 53.5, $J_{CH} = 113$, $J_{CP} = 7$, $J_{CW} = 80$ Hz), a neopentylidene ligand ($\delta(C_\alpha)$ 286, $J_{CH} = 90$, $J_{CP} = 14$, $J_{CW} = 120$ Hz), a neopentylidyne ligand ($\delta(C_\alpha)$ 316, $J_{CP} = 14$, $J_{CW} = 210$ Hz), and two equivalent PMe_3 ligands (confirmed by ^{31}P NMR). The neopentylidene α proton is found at τ 1.85 (t, $J_{HP} = 2.9$ Hz) and the neopentyl α proton at τ 8.78 (t, $J_{HP} = 18$ Hz) in the ^1H NMR spectrum.[18] Neither spectrum changes on heating the sample to 80 °C; evidently the three hydrocarbon ligands *do not interconvert* on the NMR time scale (cf. $\Delta G^\ddagger = 28$ kcal for α-hydrogen scrambling in $Ta(CH_2CMe_3)_3(CHCMe_3)$[19]). The mass spectrum of **3** is consistent with its formulation but is not simple.[20] **3** begins to decompose at ~110 °C in toluene and does not sublime without decomposition. Since the reaction of **1** with PMe_2Ph proceeds much more slowly than the reaction with PMe_3, we suggest that phosphine coordinates to the $(Me_3CCH_2)_3M\equiv CCMe_3$ monomer to give a five-coordinate species from which neopentane is lost more readily (cf. the preparation of $M(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$ from $M(CH_2CMe_3)_3$-$(CHCMe_3)$; M = Nb or Ta[1]).

The structure of $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)$-$(PMe_3)_2$ is believed to be analogous to those of $M(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$[1] (M = Nb or Ta) since the phosphine ligands are equivalent in each case and the neopentyl H_α-P coupling constants are identical (18 Hz). The proposed trigonal bipyramid (eq 2; all C_5H_y ligands lie in the

$(Me_3CCH_2)_3W\equiv CCMe_3 + 2PMe_3 \longrightarrow CMe_4$

$$+ \quad X-W \quad (2)$$

3
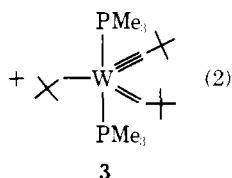
pseudotrigonal plane) is based on preliminary X-ray data for $Ta(CHCMe_3)_2(mesityl)(PMe_3)_2$ which suggest it has axial PMe_3 ligands.[21]

The reaction of **1** with 1 mol of dmpe ($Me_2PCH_2CH_2PMe_2$) in toluene (1 h, 110 °C) gives neopentane and a monomeric complex[22] whose properties resemble those of **3**. Its $^{13}C\{^1H\}$ spectrum[23] shows a neopentyl (δ 54.7), a neopentylidene (256), and a neopentylidyne (296) ligand, but its structure must be different since dmpe can only span sites 90° apart. If we postulate that π-bonding C_5H_y ligands ($y = 10$ or 9) prefer equatorial sites, then a likely structure is **4** (eq 3).

On further heating with dmpe, **4** (but not **3**) loses 1 mol of *trans*-di-*tert*-butylethylene (identified by ^1H and ^{13}C NMR and GLC) and gives yellow, crystalline $W(dmpe)_2(C_5H_{10})$ quantitatively. Although the precise nature of this species has so far eluded us,[24] we can at least propose that a tris(neopentylidene) intermediate *is* accessible, but only from **4**, not

$(Me_3CCH_2)_3W\equiv CCMe_3 + dmpe \longrightarrow$

$$\text{(3)}$$

4
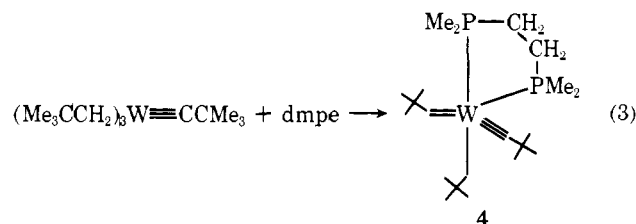
from **3**, and that two neopentylidene ligands in this intermediate combine intramolecularly to form the olefin which is then displaced by dmpe.

Analogous reactions of **2** are comparatively sluggish and compounds analogous to **3** and **4** have not been observed.

References and Notes

(1) Part 11: J. D. Fellmann, G. A. Rupprecht, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 5964 (1978).

(2) For reviews, see R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.*, **4**, 155 (1975), or N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew, Chem., Int. Ed. Engl.*, **15**, 401 (1976).

(3) The tungsten product is a greenish gold crystalline complex which is soluble and stable for several hours in ether or benzene in the absence of oxygen or moisture, but which decomposes rapidly in the solid state at 25 °C to a blue oil. Chloride analyses and GLC determination of ether suggest the formulation WCl_5(ether). The organic products are 2,2,5,5-tetramethylhexane (33%), neopentane (14%), and neopentyl chloride (3%); this accounts for 83% of the neopentyl group.

(4) S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs, and M. R. Churchill, *J. Am. Chem. Soc.*, **100**, 5962 (1978).

(5) For **1**, mol wt = 644 at 0.0344 M and 743 at 0.0120 M or mol wt = 700 ± 50; calcd for dimer, 932. For **2** mol wt = 759 at 0.0085 M, 835 at 0.0077 M, and 643 at 0.0120 M or 750 ± 100; calcd mol wt = 756. Since the experimental error in this cryoscopic method is on the order of 10% we cannot be certain at this time that the molecular weight measurably depends on the concentration in this range (solvent, cyclohexane).

(6) The ratio of the relatively weak peaks at m/e 462, 463, 464, and 466 is 2:1:2:2, as expected (26:14:31:28) for **1** containing ^{182}W, ^{183}W, ^{184}W, and ^{186}W, respectively. The first fragment which is lost is not H, but $Me_2C\equiv CH_2$, giving a continually more complex pattern starting at m/e 410. The seven-line pattern observed for **2**, is similarly consistent with its formulation.

(7) (a) The structure of $[Nb(CH_2SiMe_3)_2(CSiMe_3)]_2$[7b] is not so symmetric as indicated by A. The Nb-C bond length differs slightly from the Nb-C' bond length and the Nb-C-Si angle is 120° (the Nb'-C-Si angle is 142°). A similar distortion is found in $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$.[7c] (b) F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1477 (1971). (c) M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, **17**, 696 (1978).

(8) (a) R. A. Anderson, A. L. Galyer, and G. Wilkinson, *Angew. Chem., Int. Ed. Engl.*, **15**, 609 (1976). (b) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **15**, 2252 (1976).

(9) M. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1120 (1973).

(10) We have attempted to add $MeC\equiv CMe$, $MeC\equiv CPh$, and $PhC\equiv CPh$ to $Mo_2(CH_2CMe_3)_6$ thermally and photochemically. Unreacted starting material was recovered in high yield in the thermal reactions.

(11) (a) Acetylenes are known to add to $[Cp(CO)_2M]_2$ (M = Mo or W) to give compounds containing a tetrahedral M_2C_2 core[11b] and an X-ray crystal structure determination of $MoCp_2(CO)_4$ (μ-EtC$\equiv$CEt) has been published.[11c] (b) R. J. Klinger, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **97**, 3535 (1975). (c) W. J. Bailey, Jr., F. A. Cotton, J. D. Jamerson, and J. R. Kolb, *J. Organomet. Chem.*, **121**, C23 (1976).

(12) (a) The ^{13}C NMR chemical shifts of the carbon atoms in the M_2C_2 core in B-type $Co_2(CO)_6$(μ-RC$\equiv$CR') molecules have been published[12b] (δ 70–95 ppm). The $^{13}C\{^1H\}$ NMR spectrum of $Mo_2Cp_2(CO)_4$(μ-MeC$\equiv$CMe) (prepared by published methods[11b]) in $CDCl_3$ showed the carbonyl carbons at δ 231, the Cp carbons at 91, the methyl carbons at 22, and the core carbons at 83. (b) S. Aime, L. Milone, R. Rossetti, and P. L. Stanghellini, *Inorg. Chim. Acta*, **22**, 135 (1977).

(13) ^{13}C NMR in C_6D_6 (gated decoupled): δ 317 (s, $J_{CW} = 230$ Hz, $CCMe_3$), 103.7 (t, $J_{CH} = 115$, $J_{CW} = 89$ Hz, CH_2CMe_3), 37.2 (s, CH_2CMe_3), 53.0 (s, $CCMe_3$), 34.6 (q, $J_{CH} = 126$ Hz, CH_2CMe_3), 32.4 (q, $J_{CH} = 123$ Hz, $CCMe_3$).

(14) (a) E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, **100**, 59 (1975); (b) F. H. Köhler, H. J. Kalder, and E. O. Fischer, *ibid.*, **113**, 11 (1976).

(15) This data would *prove* that monomer-dimer interconversion is fast on the ^{13}C NMR time scale only if we could be certain that the relaxation time of the neopentylidyne C_α in the dimer is the same as in the monomer (which is not likely) or that the spectrum was run under conditions where both would have relaxed completely between pulses. The area of the $^{183}W\equiv C_\alpha$ satellite peaks in a monomer should be 14.4% of the total C_α peak area, but in a dimer with a bridging neopentylidyne ligand the C_α satellite peaks should be 26.5% of the total C_α area.

(16) ^{13}C NMR in C_6D_6: δ 324 (s, CCMe$_3$), 88.2 (t, J_{CH} = 111 Hz, CH$_2$CMe$_3$), 53.8 (s, CCMe$_3$), 34.1 (q, J_{CH} = 125 Hz, CMe$_3$), 33.6 (s, CH$_2$CMe$_3$), 30.3 (q, J_{CH} = 125 Hz, CMe$_3$).

(17) ^{13}C NMR in C_6D_6: δ 316 (J_{CP} = 14, J_{CW} = 210 Hz, CCMe$_3$), 286 (J_{CH} = 90, J_{CP} = 14, J_{CW} = 120 Hz, CHCMe$_3$), 53.5 (J_{CH} = 113, J_{CP} = 7, J_{CW} = 80 Hz, CH$_2$CMe$_3$), 52.4 (CMe$_3$), 47.0 (CMe$_3$), 38.3 (J_{CH} = 120 Hz, CMe$_3$), 34.3 (CMe$_3$), 33.4 (J_{CH} = 125, J_{CP} = 3 Hz, CMe$_3$), 32.6 (J_{CH} = 125, J_{CP} = 3 Hz, CMe$_3$), 22.0 (J_{CH} = 126, J_{CP} = 15 Hz, PMe$_3$).

(18) ^{1}H NMR in C_6D_6 at 270 MHz: τ 1.85 (t, 1, J_{HP} = 2.9 Hz, CHCMe$_3$), 8.62 (t, 18, J_{HP} = 3.3 Hz, PMe$_3$), 8.74 (s, 9, CMe$_3$), 8.75 (s, 9, CMe$_3$), 8.76 (s, 9, CMe$_3$), 8.78 (t, 2, J_{HP} = 18 Hz, CH$_2$CMe$_3$). On decoupling ^{31}P, all triplets sharpen to singlets.

(19) R. R. Schrock and J. D. Fellmann, *J. Am. Chem. Soc.*, **100**, 3359 (1978).

(20) The *m/e* 546 parent ion is not seen. A typical pattern starting at *m/e* 477 corresponds to loss of a neopentyl group. It overlaps with a pattern about one fifth as intense starting at *m/e* 478 which *formally* corresponds to loss of a neopentylidene fragment from *m/e* 548.

(21) M. R. Churchill and W. J. Youngs, private communication.

(22) Calcd: 544. Found in cyclohexane: 531 (concentration, 0.033 M).

(23) ^{13}C{^{1}H} NMR in C_6D_6: δ 296 (t, $J_{CP} \approx J_{CP'} \approx$ 12 Hz, CCMe$_3$), 256 (dd, J_{CP} = 13, $J_{CP'}$ = 31 Hz, CHCMe$_3$; J_{CH} = 84 Hz in the gated spectrum), 54.7 (t, $J_{CP} \approx J_{CP'}$ = 4 Hz, CH$_2$CMe$_3$), 51.7 (s, CMe$_3$), 47.7 (s, CMe$_3$), 34.0 (s, CMe$_3$), 36.4 (s, CMe$_3$), 34.6 (s, CMe$_3$), 33.0 (t, $J_{CP} \approx J_{CP'}$ = 3, CMe$_3$). The dmpe carbon atoms give rise to a complex non-first-order pattern from 32 to 12 ppm.

(24) Two likely possibilities are a neopentylidene or a neopentylidyne hydride complex (no ν_{MH} is obvious in the IR spectrum). An extremely broad low-field resonance can be seen after exhaustive pulsing. All P nuclei may be different and/or the molecule may be fluxional. Variable-temperature and ^{31}P decoupling experiments are in progress.

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Figure 1. UV-visible spectra of Ag$_{1,2,3}$/Ar mixtures (Ag/Ar $\simeq$ 1/10^3) at 12 K. Note the growth of Ag$_2$ and Ag$_3$ clusters and loss of Ag atoms as a result of 305-nm Ag atom excitation. Spectra A, B, and C represent irradiation times of 0, 1, and 4 min, respectively.

Relative Extinction Coefficient Measurements for Naked Silver Atom Clusters, Ag$_{1,2,3}$, by Photoaggregation Techniques

Sir:

Ligand-free molecular clusters containing only several transition metal atoms are currently becoming accessible for detailed spectroscopic and chemical studies.[1] Naked molecular clusters are of considerable interest in a wide area which includes both homogeneous and heterogeneous catalysis. In particular, one may think in terms of modeling the active centers of highly dispersed heterogeneous catalysts, using very small metal atom clusters of variable but precisely defined size. Another attractive proposition is that the electronic structure of metal atom cluster complexes, which are often active homogeneous catalysts, may be elucidated through combined experimental and theoretical studies of the corresponding metal atom framework.

We have reported a cryochemical preparative route to transition metal atom clusters, involving photoinduced diffusion and aggregation of matrix-isolated metal atoms, monitored by ultraviolet-visible absorption spectroscopy.[2] In this communication we report an application of this technique to the measurement of molar extinction coefficients, relative to atomic species, for diatomic and triatomic silver.

Extinction coefficient information is of fundamental importance in quantitative studies of the chemistry and photochemistry of transition metal atom clusters, and in the analysis of metal atom recombination kinetics. Relative extinction coefficients for transition metal diatomic molecules, $\epsilon_{M_2}/\epsilon_M$, as determined by quantitative metal atom deposition studies, have been reported.[3] However, we would suggest that the controlled photoaggregation technique allows for a more convenient and accurate evaluation of these quantities. Moreover, an extension of this technique to higher clusters is also possible.
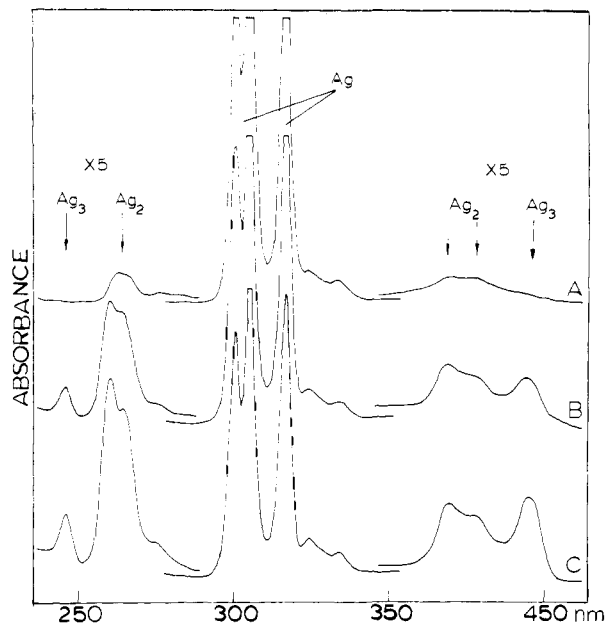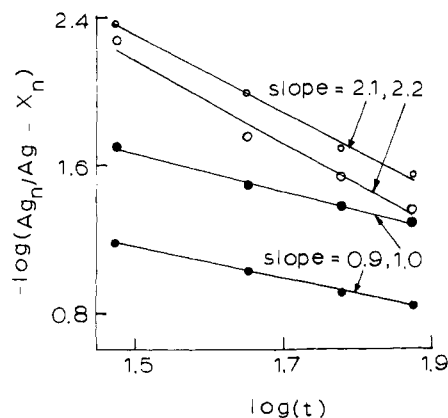

Figure 2. Kinetic plots showing a linear dependence on irradiation time (305 nm) of the absorbance ratios Ag$_2$^{263nm}/Ag^{300nm} and Ag$_2$^{390nm}/Ag^{300nm} (O) and a linear dependence on the square of irradiation time of the absorbance ratios Ag$_3$^{245nm}/Ag^{300nm} and Ag$_3$^{440nm}/Ag^{300nm} (●), as predicted from the simple kinetic analysis. The quantities X_n were chosen in order to shift the Ag$_2$/Ag vs. t and Ag$_3$/Ag vs. t^2 plots through the origin. Details will be described in the full paper.

The cryophotoclustering technique is illustrated for Ag atoms in Figure 1. Kinetic studies of the clustering process are now in progress and the results will be described in detail in a forthcoming publication. Preliminary results have indicated that, under certain conditions, the rates of formation of diatomic and triatomic silver may usefully be approximated by simple second-order kinetics. A simple analysis predicts that the slope of a log (Ag$_n$/Ag) vs. log (t) plot, where Ag$_n$ and Ag represent absorbances and t represents the irradiation time, should have a value of 1.0 for n = 2 and 2.0 for n = 3. These plots are shown in Figure 2. The observed slopes, 0.9/1.0 and 2.1/2.2 support our Ag$_2$ and Ag$_3$ assignments, which are indicated in Figure 1. These assignments correlate exactly with earlier assignments based on Ag atom concentration experiments.[2a]

Simple mass-balance considerations lead to the following expression which relates the decrease in an atomic absorption