

form and the related chair and half-chair forms are allowed. The locally symmetric compounds (VI, X = O, CH₂, CMe₂) each show a single negative CD band. For the ethylidene isomers a torsion couplet is superimposed on this negative band (at *ca.* 202 nm in this case).¹⁴ We suggest that this represents the first experimental evidence for the location of the $\sigma_a \rightarrow \pi_x^*$ transition of olefins. The $\sigma_a \rightarrow \pi_x^*$ transition should be highly dissymmetric but only a minor contributor to the absorption spectrum.

Thus four transitions can contribute to the CD spectra of olefins in the 185–225-nm energy span. For trisubstituted olefins CD bands appear in the following sequence: $\pi_x \rightarrow 3s$ (225–190 nm, solvent dependent), $\pi_x \rightarrow \pi_x^*$ (200–210 nm), $\sigma_a \rightarrow \pi_x^*$ (195–205 nm), and $\pi_x \rightarrow \pi_y^*$ (185–200 nm). In light of the enhanced separation observed in couplets, the last three transitions very likely occur within 10 nm.

The extreme complexity of this spectral region argues against strict use of any simple rule. Apparently the success of the Scott–Wrixon dissignate² octant rule and the APB model owes to the sign correspondence for the low energy portion of the torsion couplet and the $\sigma_a \rightarrow \pi_x^*$ transition in certain common olefin types (C₂-twist cyclohexenes and exomethylenecyclopentanes). At this juncture only the use of strictly analogous models can be fully justified.

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(14) The argument that this negative contribution is another transition runs as follows. Assuming that vinylic substitution does not change the relative energy of the π_x^* and π_y^* transitions, a rotatory contribution due to the dissymmetric substituent array represented by the skeleton (but unrelated to torsion) should influence only one portion of the couplet. In fact, the negative portion of the couplet is dominant independent of its relative energy. Even if the stated assumption were proven this argument would not be conclusive since we have not allowed for vibronic detail or variation in λ_{max} for conformational isomers.

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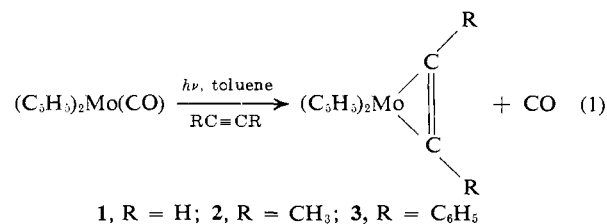
Photogeneration of Coordinatively Unsaturated Sandwich Compounds of Molybdenum and Tungsten from Their Carbonyl Complexes

Sir:

In a search for convenient avenues toward generation and study of coordinatively unsaturated complexes, we have observed that the transient species (C₅H₅)₂Mo and (C₅H₅)₂W^{1,2} are produced most conveniently by photolysis of their respective monocarbonyl complexes. Irradiation of toluene solutions of (C₅H₅)₂Mo(CO) at either -78° or at room temperature (high-pressure mercury lamp, 450 watt, Pyrex filter) for 4–16 hr in the presence of alkynes resulted in the formation of the respective alkyne complexes in essentially quantitative yields (eq 1). The corresponding ethylene

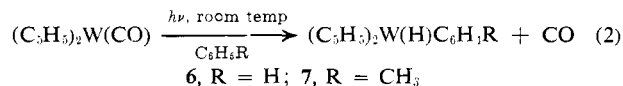
(1) J. L. Thomas, *J. Amer. Chem. Soc.*, **95**, 1838 (1973).

(2) J. L. Thomas and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1386 (1972).



(4) and acrylonitrile (5) complexes¹ were obtained analogously in the presence of the respective alkenes. These products, some of which (2–5) have been previously synthesized^{1–3} by other methods, are obtained virtually without side products by this photochemical method. The novel, unsubstituted acetylene complex 1 sublimates as an orange solid at 30° (10⁻³ Torr) and is characterized by singlets at τ 5.70 and 2.32 in its ¹H nmr (integrated intensities 10:1.9), a C=C stretching band at 1613 cm⁻¹, and a mass spectrum with peaks at *m/e* 256 (parent ion) and 230 ((C₅H₅)₂Mo⁺). The thermal stability of this complex is most unusual for a mononuclear, unsubstituted acetylene complex (*cf.* ref 4) and is undoubtedly related to the unusually strong reduction of C–C bond orders in molybdenocene π -complexes.¹ In the absence of suitable substrate molecules, photolysis of toluene solutions of (C₅H₅)₂Mo(CO) yields only insoluble materials of undetermined composition, containing possibly some polymeric [(C₅H₅)₂Mo]_{*n*}.^{1,2}

In contrast to this, benzene or toluene solutions of the tungstenocene carbonyl complex (C₅H₅)₂W(CO) give essentially quantitative yields of the corresponding aryl hydride compounds 6 and 7 when photolyzed in the absence of alkene or alkyne substrates (eq 2).⁵



Obviously, the photogenerated species (C₅H₅)₂W undergoes a facile insertion into the C–H bonds of aromatic solvent molecules, reminiscent of that of related niobium and tantalum complexes.⁶ In the presence of both, arene solvent and alkyne substrate (*ca.* 1 M), comparable amounts of alkyne addition (2) and arene insertion (7) products are obtained from photolysis of (C₅H₅)₂W(CO),⁷ indicating that addition to C≡C bonds is only slightly favored over insertion to C–H bonds for tungsten, whereas in the molybdenum system the former is observed exclusively. Possible factors contributing to this gradation in carbene-like reactivity between otherwise largely analogous group VI metal complexes, and evidence concerning the role of ground- and excited-state intermediates in these reactions, will be presented in a forthcoming, more detailed account.

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(5) (C₅H₅)₂W(H)C₆H₄R (R = H, CH₃) can be prepared by heating (C₅H₅)₂WH₂ in arene in the presence of isoprene or from the photolysis of (C₅H₅)₂WH₂ in arenes: M. L. H. Green and P. J. Knowles, *J. Chem. Soc. A*, 1508 (1971); C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1114 (1972); nmr and mass spectra of compounds 6 and 7 are in accord with these reports.

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(7) Pure (C₅H₅)₂W(C₂(CH₃)₂) (2) is prepared by photolyzing the tungstenocene monocarbonyl in liquid 2-butyne at -78°; in the reaction mixture, compounds 2 and 7 are identified and their ratios estimated by nmr.

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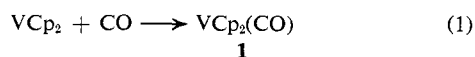
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**Carbonyl Complexes of
Bis(cyclopentadienyl)vanadium(II) and
Bis(cyclopentadienyl)vanadium(III).
Bis(cyclopentadienyl)iodovanadium(III), a Model
Compound for the Quantitative Assessment of the
Reversible Carbon Monoxide Coordinative Addition**

Sir:

Bis(cyclopentadienyl)vanadium(II), VCp_2 , was reported to react with carbon monoxide¹ or, better, with CO-H_2 ² to give $\text{VCp}(\text{CO})_4$. The reaction³ between VCp_2 and $\text{V}(\text{CO})_6$ in the presence of CO at atmospheric pressure yields the salt-like compound $[\text{VCp}_2(\text{CO})_2][\text{V}(\text{CO})_6]$, containing the cation $[\text{VCp}_2(\text{CO})_2]^+$, iso-electronic with $\text{TiCp}_2(\text{CO})_2$.^{4,5}

We have now found that VCp_2 reacts with carbon monoxide under mild conditions.



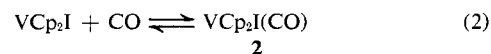
Gas volumetric measurements have shown that reaction 1 is fast (about 10 min for a $5.34 \times 10^{-2} M$ solution of VCp_2 in toluene at 25° at atmospheric pressure of CO) and substantially quantitative. For preparative purposes, $\text{VCp}_2(\text{CO})$ can be obtained by carbonylation of VCp_2 in heptane at 25° for about 10 min, followed by cooling at -10° (80.9% yield). The monocarbonyl of vanadium(II) is a deep brown solid, very sensitive to air.

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{OV}$ (209.14 g/mol): C, 63.17; H, 4.82. Found: C, 63.50; H, 5.02; mol wt 202 (cryoscopy in benzene). The infrared spectrum has one single C–O stretching vibration at 1881 cm^{-1} (toluene), consistent with the formulation of this compound as a monomeric monocarbonyl. The magnetic susceptibility is 1330×10^{-6} cgs (including the diamagnetic correction = 159×10^{-6} cgs) corresponding to $\mu_{\text{eff}} = 1.76$ BM. This value is consistent with the fact that the number of valence electrons⁶ is 17 in this mononuclear compound. The low value of the C–O stretching vibration is quite common for bent bis-cyclopentadienyl systems of d^2 – d^4 configurations. For example, the following infrared absorptions were reported: $\text{TiCp}_2(\text{CO})_2$ ⁵ (1975 and 1897 cm^{-1}), $\text{MoCp}_2(\text{CO})_2$ ⁷ (1905 cm^{-1}), and $\text{WCp}_2(\text{CO})_2$ ⁸ (1864 cm^{-1}). The considerable amount of back-donation suggested by these low wave

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number values is in agreement with the basic properties of the metal center which are now well substantiated in these systems both experimentally⁹ and theoretically.¹⁰

Bis(cyclopentadienyl)iodovanadium(III),¹¹ VCp_2I ($\mu_{\text{eff}} = 2.81$ BM at room temperature, mol wt = 311, calcd 308.04 g/mol, by cryoscopy in benzene), reacts with CO



The iodo carbonyl derivative has one single C–O stretching vibration at 1953 cm^{-1} (toluene solution), corresponding to a 72 cm^{-1} increase with respect to $\text{VCp}_2(\text{CO})$, which is consistent with the increased oxidation state of the central metal atom. Compound 2 is monomeric in benzene solution as shown by the fact that, all else being equal, the freezing point depression observed for VCp_2I in benzene under nitrogen¹² was the same as that under carbon monoxide. Equilibrium 2 is rapidly established, and the equilibrium constants were measured gas volumetrically at temperatures between 272 and 316°K. The results are in Table I and the following thermodynamic values were obtained:

Table I. Equilibrium Data^a for the Reaction
 $\text{VCp}_2\text{I} + \text{CO} \rightleftharpoons \text{VCp}_2\text{I}(\text{CO})$

T , °K	$10^3[\text{CO}]$, M	$10^{-2}K$, M^{-1}
272	7.28	8.46
282	7.39	4.06
295	7.47	1.49
308	7.44	0.56
316	7.31	0.30

^a In toluene as solvent at the total (CO + vapor of the solvent) constant pressure of 1 atm. The concentration of CO was experimentally determined from 286 to 314°K and extrapolated to the other temperatures.

$\Delta H^\circ = -13.1 \pm 1.0$ kcal/mol; $\Delta S^\circ = -34.6 \pm 3.4$ eu.

It is interesting to compare our values with the corresponding thermodynamic quantities reported by Vaska¹³ for the addition of CO to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ($\Delta H^\circ = -10.8$ kcal/mol; $\Delta S^\circ = -22$ eu). The two systems are, however, largely different since in our case spin pairing has to take place upon carbonylation, contrary to the iridium(I) system. This may be compensated by the lower amount of molecular rearrangement required in our case, thus yielding similar ΔH° values.

Bis(cyclopentadienyl)iodocarbonylvanadium(III) was isolated in admixtures with VCp_2I , since partial decarbonylation always occurred. However, a mixture of $\text{VCp}_2\text{I}(\text{CO})$ and VCp_2I of known composition (91:9% by weight, respectively) was isolated and eq 2 was also verified by decarbonylation of $\text{VCp}_2\text{I}(\text{CO})$. The magnetic susceptibility of this mixture could satisfactorily be explained by assuming that $\text{VCp}_2\text{I}(\text{CO})$ is diamagnetic, as expected.

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