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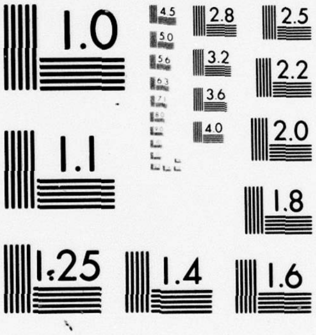

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Irradiation of $Mo(CO)_6$ in the presence of C_5H_6 yields $(\eta^5-C_5H_5)(\eta^3-C_5H_7)-Mo(CO)_2$ via a sequence of light-induced reactions involving substitution, $Mo(CO)_n(C_5H_6)$ (n = 5,4); oxidative addition, $(\eta^5-C_5H_5)Mo(CO)_3H$; and hydrometallation, $(\eta^5-C_5H_5)(\eta^3-C_5H_7)Mo(CO)_2$. The sequence of events can be followed by monitoring the infrared spectral changes in the CO stretching region. An authentic sample of $(\eta^5-C_5H_5)Mo(CO)_3H$ cleanly yields $(\eta^5-C_5H_5)(\eta^3-C_5H_7)Mo(CO)_2$ when irradiated in the presence of C_5H_6; the 355 nm quantum yield for this reaction is 0.12 ± 0.02. Photoinduced hydrometallation of $C_5(CH_3)_5H$,

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Photoreaction of Hexacarbonylmolybdenum(0) and Tricarbonyl(η^5-cyclopentadienyl)hydridomolybdenum(II) in the Presence of Cyclopentadiene: Substitution, Oxidative Addition, and Hydrometallation

by

10 William C. Mills, III [redacted] Mark S. Wrighton

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trans-trans-2,4-hexadiene, 1,4-pentadiene, trans-1,3-pentadiene also appears to obtain upon irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ in the presence of the diene. Irradiation of $Cr(CO)_6$ in the presence of C_5H_6 yields $Cr(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)$.

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Photoreaction of Hexacarbonylmolybdenum(0) and Tricarbonyl(η^5-cyclopentadienyl)hydridomolybdenum(II) in the Presence of Cyclopentadiene: Substitution, Oxidative Addition, and Hydrometallation

Abstract: Irradiation of $Mo(CO)_6$ in the presence of C_5H_6 yields $(\eta^5-C_5H_5)(\eta^3-C_5H_7)Mo(CO)_2$ via a sequence of light-induced reactions involving substitution, $Mo(CO)_n(C_5H_6)$ (n = 5,4); oxidative addition, $(\eta^5-C_5H_5)Mo(CO)_3H$; and hydrometallation, $(\eta^5-C_5H_5)(\eta^3-C_5H_7)Mo(CO)_2$. The sequence of events can be followed by monitoring the infrared spectral changes in the CO stretching region. An authentic sample of $(\eta^5-C_5H_5)Mo(CO)_3H$ cleanly yields $(\eta^5-C_5H_5)(\eta^3-C_5H_7)Mo(CO)_2$ when irradiated in the presence of C_5H_6; the 355 nm quantum yield for this reaction is 0.12 ± 0.02. Photoinduced hydrometallation of $C_5(CH_3)_5H$, trans-trans-2,4-hexadiene, 1,4-pentadiene, trans-1,3-pentadiene also appears to obtain upon irradiation of $(\eta^5-C_5H_5)Mo(CO)_3H$ in the presence of the diene. Irradiation of $Cr(CO)_6$ in the presence of C_5H_6 yields $Cr(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$.

Photoreaction of Hexacarbonylmolybdenum(0) and Tricarbonyl(η^5-cyclopentadienyl)hydridomolybdenum(II) in the Presence of Cyclopentadiene: Substitution, Oxidative Addition, and Hydrometallation

Sir:

We wish to report new results pertaining to photoreaction of low-valent metal carbonyls in the presence of olefins. The systems reported on here are $Mo(CO)_6$ and $(\eta^5-C_5H_5)Mo(CO)_3H$ irradiated in the presence of cyclopentadiene, C_5H_6. These particular systems are important inasmuch as $Mo(CO)_6$ is a known catalyst precursor under photochemical conditions for the isomerization of olefins[1] and 1,4-hydrogenation of 1,3-dienes,[2] and $(\eta^5-C_5H_5)Mo(CO)_3H$ is reported to be a stoichiometric reducing agent for converting 1,3-dienes to alkenes.[3] Further, C_5H_6 is a source of $\eta^5-C_5H_5$ in metal complexes, when reacted with an appropriate precursor. Generally, using light to effect an individual step in a catalytic or stoichiometric process may provide for greater specificity or rate or change the course of events altogether. In the systems under consideration here, Mo-CO dissociation is likely a thermally rate limiting process at room temperature which can be substantively altered by optical excitation.[4,5]

Our first interest in the $Mo(CO)_6/C_5H_6$ system actually began some years ago when we attempted the photoassisted 1,4-hydrogenation of C_5H_6 to cyclopentene under the conditions[2] giving efficient hydrogenation of those 1,3-dienes which can easily achieve, or are held in, an *s-cis* conformation. Little catalytic chemistry occurred using $Cr(CO)_6$ the catalyst precursor in the attempted hydrogenation of C_5H_6, though large spectral changes obtained upon irradiation. We now present the results of a study of the irradiation of $Mo(CO)_6$ or $Cr(CO)_6$ in the presence of C_5H_6. Irradiation (355 ± 20 nm, 2×10^{-6} ein/min) at 25°C of 5×10^{-3}M $Mo(CO)_6$ in a degassed isooctane solution of freshly distilled 0.1M C_5H_6 rapidly yields chemical reaction which can be monitored by ir spectroscopy in the CO-stretching region. In accord with very early findings associated with irradiation of $M(CO)_6$ (M = Cr, Mo, W) in the presence of olefins,[6] the ir spectral changes initially correspond to formation of $Mo(CO)_5(\eta^2\text{-}C_5H_6)$ with ir bands as given in Table I, equation (1). This primary photoproduct, however, absorbs in the near-uv

$$Mo(CO)_6 \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} Mo(CO)_5 + CO \xrightarrow{C_5H_6} Mo(CO)_5(\eta^2\text{-}C_5H_6) \qquad [1]$$

and is itself photosensitive under the conditions used to produce it.

Continued irradiation of the $Mo(CO)_6$ / $Mo(CO)_5(\eta^2\text{-}C_5H_6)/C_5H_6$ mixture results in the further decline of $Mo(CO)_6$ and growth of other Mo-carbonyl species. Ir bands of greater and lesser importance appear at 2043(w), 2029(w), 1961(s), and 1912(w), cm^{-1} and ultimately, two prominent features at 1880 and 1950 cm^{-1} appear. The strong 1961 cm^{-1} feature is attributable to trans-$Mo(CO)_4(\eta^2\text{-}C_5H_6)_2$ on the basis of its intensity dependence in time and the fact that trans-$Mo(CO)_4(\eta^2\text{-}1,3\text{-butadiene})_2$ has a similar feature at 1965 cm^{-1}.[6] The bands at 2043 and 1912 cm^{-1} may be due to $Mo(CO)_4(\eta^4\text{-}C_5H_6)$ or to cis-$Mo(CO)_4(\eta^2\text{-}C_5H_6)_2$; presumably the other two features for such complexes[7] in the 1965-1940 cm^{-1} range are obscured by the 1961 and 1957 cm^{-1} absorptions of trans-$Mo(CO)_4(\eta^2\text{-}C_5H_6)_2$ and $Mo(CO)_5(\eta^2\text{-}C_5H_6)$, respectively. The weak band at 2029 cm^{-1} identically matches the highest energy CO-stretching absorption of an authentic sample of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$[8], but the 1946 cm^{-1} band of this complex is obscured. The bands at 1950 and 1880 cm^{-1} identically match those from an authentic sample of $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$.[9] This product is somewhat photosensitive, and it, too, ultimately reacts. Yields of up to ~20% (based on ir absorption) of $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$ can be realized starting with $Mo(CO)_6$. Interestingly, the irradiation of $Cr(CO)_6$ in the presence of C_5H_6 results in ir bands at 1942 and 1880 cm^{-1} which we attribute to $Cr(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$.[10] The formation of such products possibly accounts for our inability to effect the 1,4-hydrogenation of C_5H_6 at 1 atm. H_2 pressure.

Equations (1)-(4) represent a plausible sequence of photochemical

$$Mo(CO)_5(\eta^2-C_5H_6) \xrightarrow{h\nu} Mo(CO)_4(\eta^4-C_5H_6) + CO \qquad (2)$$

$$Mo(CO)_4(\eta^4-C_5H_6) \xrightarrow{h\nu} (\eta^5-C_5H_5)Mo(CO)_3H + CO \qquad (3)$$

$$(\eta^5-C_5H_5)Mo(CO)_3H + C_5H_6 \xrightarrow{h\nu} Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7) + CO \qquad (4)$$

reactions leading to the formation of the $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$. Irradiation of <u>trans</u>-$Mo(CO)_4(\eta^2-C_5H_6)_2$ may also give rise to this product; isolation and characterization of both tetracarbonyl species is of interest. But whatever the mechanism, the product reflects the fact that C_5H_6 binds, oxidatively adds, and undergoes hydrometallation. The reactive, doubly allylic C-H bonds and the stability of $\eta^5-C_5H_5$ complexes promotes the formation of the $(\eta^5-C_5H_5)Mo(CO)_3H$ upon photogeneration of coordinatively unsaturated intermediates in the presence of C_5H_6.

Irradiation of an authentic sample of $(\eta^5-C_5H_5)Mo(CO)_3H$[11] in the presence of C_5H_6 leads to the clean formation of $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$[12] according to equation (4). Inasmuch as the hydride is conveniently synthesized, equation (4) represents the synthetic procedure of choice for $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$. The 355 nm quantum yield is 0.12 ± 0.02. Figure 1 shows the ir spectral changes accompanying a typical photoreaction. We conclude that the formation of product proceeds via photogeneration of $(\eta^5-C_5H_5)Mo(CO)_2H$ followed by thermal reaction with C_5H_6. An alternative mechanism involving $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radicals as in the simple substitution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$[13] appears to be ruled out by the following experiment. Visible light (514.5 nm) irradiation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ in the presence of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ and C_5H_6 does not lead to $Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)$. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ is a known photochemical source of $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radicals.[14] Irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ in the presence of other dienes such as trans-1,3-pentadiene, trans,trans-2,4-hexadiene, 1,4-pentadiene, and 1,2,3,4,5-pentamethylcyclopentadiene results in ir spectral changes consistent with the formation of $Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-allyl})$ complexes. Establishing the role of such complexes in the formation of alkenes from 1,3-dienes using $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ is the object of continuing studies in this laboratory.

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__Table I.__ Infrared Spectral Band Maxima for Pertinent Complexes.

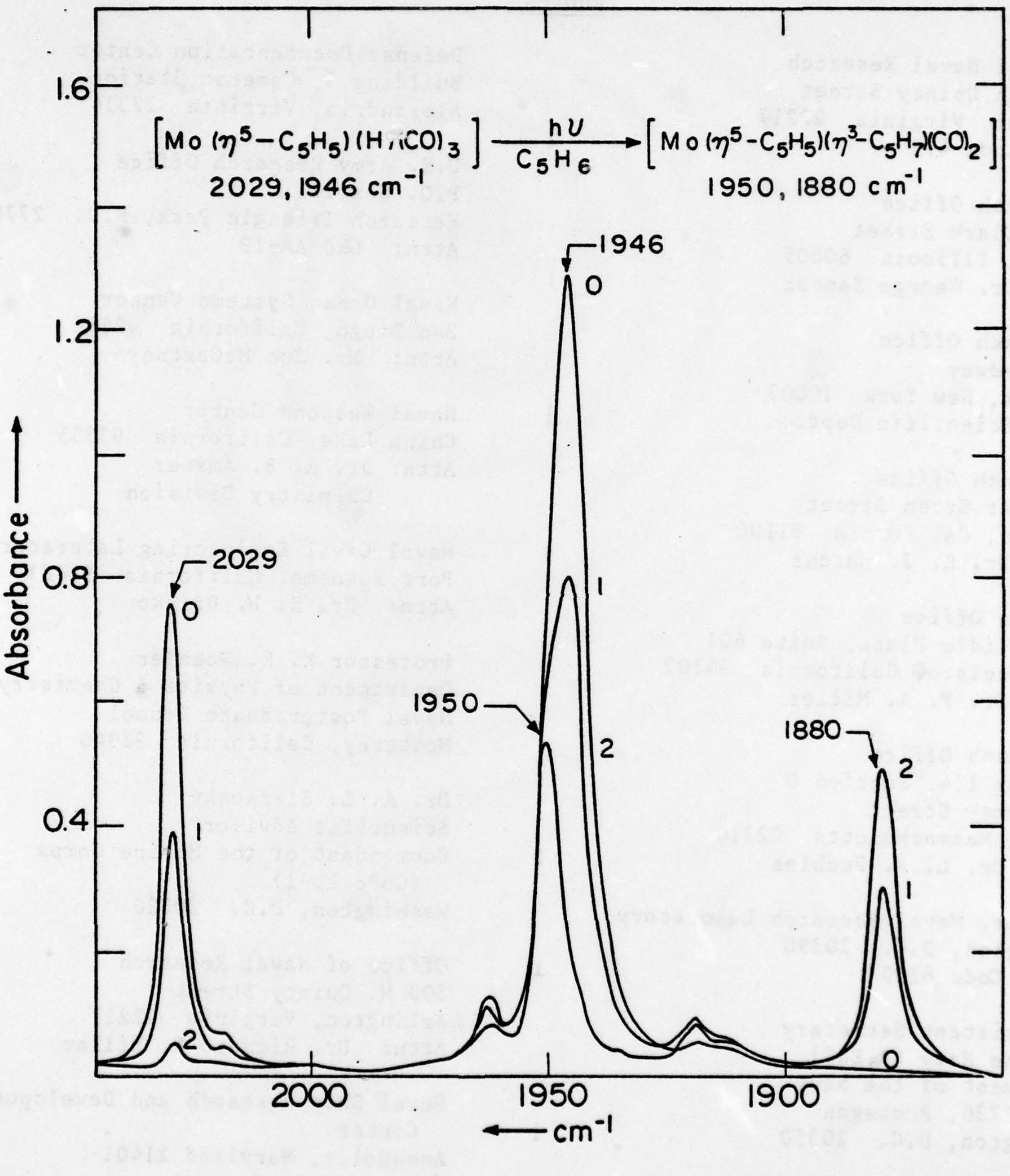
Complex	Band Maxima, cm^{-1} (ε, $\underline{M}^{-1}cm^{-1}$)[a]
$Mo(CO)_6$	1988 (53,800)
$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$	2029 (5340); 1946 (9190)
$Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)$	1950 (6290); 1880 (6010)
$Mo(CO)_5(\eta^2\text{-}C_5H_6)$	2079 ($\underline{\ 1\ }$); 1957 ($\underline{\ 8\ }$); 1944 ($\underline{\ 4\ }$)
__trans__ $-Mo(CO)_4(\eta^2\text{-}C_5H_5)_2$	1961 (---)
$Cr(CO)_6$	1987 (51,700)
$Cr(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)$	1942 ($\underline{1.14}$); 1880 ($\underline{1.0}$)

---

[a] All data recorded at 25°C in alkane solvent employing a Perkin Elmer 180 ir spectrometer. Numbers in parentheses which are underlined represent relative absorbance for that complex.

Figure Caption

Figure 1. Infrared spectral changes accompanying 355 ± 20 nm irradiation (2 x 10^{-6} ein/sec) of degassed 1.0 ml isooctane solutions of 1.4 x 10^{-2} $\underline{M}$ $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ and 0.6$\underline{M}$ C_5H_6. Trace 0 was before exposure to the irradiation and curves 1 and 2 are after 0.5 and 4.0 h of irradiation, respectively. Ir spectra were recorded in 0.1 mm pathlength NaCl cells.


[Mo(η^5-C_5H_5)(H)(CO)$_3$] $\xrightarrow[C_5H_6]{h\nu}$ [Mo(η^5-C_5H_5)(η^3-C_5H_7)(CO)$_2$]
2029, 1946 cm^{-1}
1950, 1880 cm^{-1}
1.6
1.2
0.8
0.4
Absorbance
2029
1946
1950
1880
0
1
2
2000
1950
1900
cm^{-1}

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