Organometallics 1982, 1, 87-94

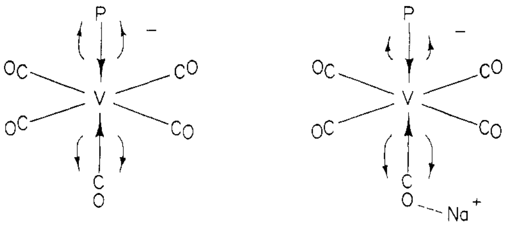

Figure 5. Competition for π density along the z axis in the symmetrical va. sodium ion perturbed $PV(CO)_5^-$.

problems are complex and the salient features only are reported here.

The displacement of PPh_3 from $V(CO)_5PPh_3^-$ was determined to be independent of entering ligand concentration (Table III) and showed a first-order dependence on the vanadium complex (eq 1 and 2). Carbon monoxide

$$PV(CO)_5^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V(CO)_5^- + P \xrightarrow{\text{excess L}} LV(CO)_5^- \qquad (1)$$

$$\text{rate} = k_1[PV(CO)_5^-] \qquad (2)$$

or $P(OPh)_3$ completely scavenged the coordinatively unsaturated $V(CO)_5^-$ anion, yielding 100% of the ligand-substituted product, $LV(CO)_5^-$.

As Table III shows, the Na^+ salt of $Ph_3PV(CO)_5^-$ undergoes P-ligand exchange with greater facility than does the less tightly interacting Et_4N^+ salt. There is less difference (possibly no *significant* difference) between the rates of reaction for the Na^+ and Et_4N^+ salts of $(n\text{-}Bu)_3PV(CO)_5^-$. The ratio of k_1 values for the $P(OPh)_3$ substitution of PPh_3 with Na^+ vs. Et_4N^+ is 2.1:1 and for the $P(OPh)_3$ substitution of $P(n\text{-}Bu)_3$ is 1.3:1.

Since the counterion effect is greater for the poorer σ-donor, better π-accepting PPh_3 ligand, we suggest that the counterion effects acts primarily through a sodium cation polarization of π-electron density as given in Figure 5. The polarization of the carbonylate in the sodium ion contact ion pair is expected to actually strengthen the $P \rightarrow V$ σ-bond donation in the absence of a substantial π-back-bonding, σ-donating synergic effect. That the bond *is* weakened supports the contention that there is a loss of V–P π-back-bonding in the species containing the good π-accepting ligand, $CO\cdots Na^+$. The greater loss of π-back-bonding is suffered by PPh_3, a better π-accepting ligand than $P(n\text{-}Bu)_3$, and hence a significant counterion effect is observed in the case of $V(CO)_5PPh_3^-$.

In agreement with all known crystal structures of alkali salts of transition-metal carbonylates in which Na^+ is contacting a carbonyl oxygen, Figure 5 shows an angular $V\text{-}CO\cdots Na^+$ linkage. The Na^+ is presumably directed by the best electrostatic potential to a site where simultaneous interaction with σ lone pair and π density is possible.[24] It is reasonable that the polarization of π-bonding electrons toward the Na^+ is the most important aspect in the enhanced donation of metal d electrons into the π^* orbitals of $CO\cdots Na^+$.

Conclusion. Infrared analysis of the ν(CO) region has determined the specific site of Na^+ interaction with C_{4v} $PV(CO)_5^-$ and $MeNCV(CO)_5^-$ to be at the carbonyl oxygen *trans* to the substituent phosphine, phosphite, or isocyanide ligand. The extent of the interaction is directly dependent on the overall electron-releasing ability of the P-donor ligands. The effect of the $Na^+\cdots OC\text{-}V$ interaction on ligand substitution is significant and positive for π-accepting ligands. The faster rates are suggested to be due to a loss of $V \rightarrow P$ π-back-bonding in the presence of $CO\cdots Na^+$, a ligand group that competes better for metal d electrons than does CO.

Acknowledgment. We appreciate the helpful conferences with D. J. Darensbourg and the financial support of the National Science Foundation Grant CHE-79-23204. The purchase of the inert atmospheres box by the Research Corp. is gratefully acknowledged. The computer-based infrared facility was supported by NSF Grant No. CHE-78-01758 to D. J. Darensbourg. We also thank Professor J. E. Ellis, University of Minnesota, for a gift of the methyl isocyanide complexes.

Registry No. $NaV(CO)_5P(n\text{-}Bu)_3$, 79152-71-9; $NaV(CO)_5PPh_3$, 79152-72-0; $NaV(CO)_5P(OPh)_3$, 79152-73-1; $NaV(CO)_5(CNMe)$, 79152-74-2; $Ph_4AsV(CO)_5(CNMe)$, 78954-00-4; $Et_4NV(CO)_5P(n\text{-}Bu)_3$, 34089-20-8; $Et_4NV(CO)_5PPh_3$, 10170-61-3; $Et_4NV(CO)_5P(OPh)_3$, 79152-75-3; $Et_4NV(CO)_5(CNMe)$, 78953-99-8.

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^{13}CO Exchange Reactions of Metal–Carbene Complexes

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Received June 9, 1981

The rate of ^{13}CO exchange with $(CO)_5Cr{=}C(OCH_3)C_6H_5$, $(CO)_5Mo{=}C(OCH_3)C_6H_5$, $(CO)_5W{=}C(OCH_3)C_6H_5$, $(CO)_5Cr{=}\overline{CO(CH_2)_2C}(CH_3)_2$, and $(CO)_5W{=}C(C_6H_5)_2$ have been measured by ^{13}C NMR spectroscopy. The rates of ^{13}CO exchange are compared with the rates of reaction of these carbene complexes with other substrates. Selective exchange of ^{13}CO into the cis position was observed for all of the metal–carbene complexes studied except $(CO)_5W{=}C(C_6H_5)_2$ which showed no stereoselectivity. The variation of the cis:trans ^{13}CO ratio was measured as a function of the extent of ^{13}CO incorporation and was used to assess whether the 5-coordinate intermediate was rigid or fluxional.

The generation of a reactive coordinatively unsaturated intermediate by the dissociation of CO from $(CO)_5M{=}CRR'$ has been suggested as a crucial step in many of the reactions of metal–carbene complexes, including thermal decomposition, phosphine substitution, hydrogenolysis, and reactions with alkenes.

The first step in the mechanism for thermal decomposition of metal–carbene complexes to carbene dimers[1] was

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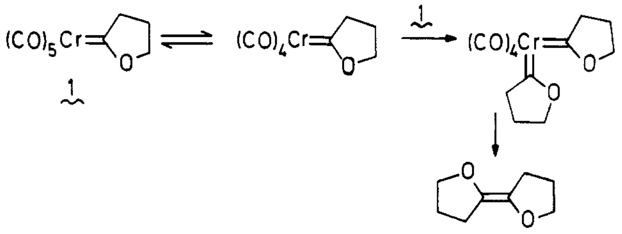
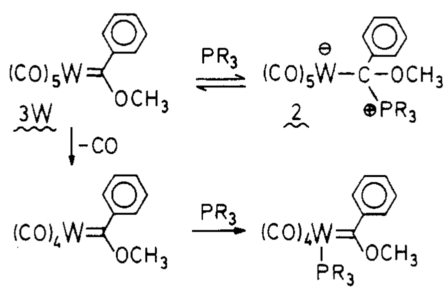
suggested to be CO dissociation.[2] Reaction of the 5-coordinate intermediate with a second molecule of starting material was suggested to result in carbene ligand transfer to form a biscarbene complex which finally decomposed to a carbene dimer. The reaction was shown not to involve free carbenes since no formation of cyclobutanone (the rearrangement product of 2-oxacyclopentylidene) was observed in thermal decomposition of pentacarbonyl(1-oxacyclopent-2-lyidene)chromium(0), 1.



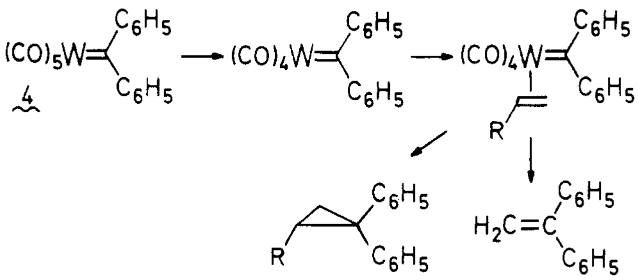
The reaction of phosphines with metal–carbene complexes at low temperature leads to zwitterionic adducts 2



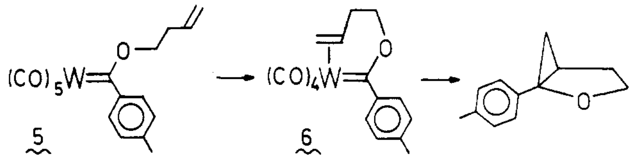
formed by addition of the phosphine to the carbene carbon atom.[3] At higher temperatures, the zwitterionic adducts 2 are in equilibrium with free phosphine and the initial carbene complex; phosphine substitution products of the carbene complex are obtained.[4] CO dissociation is a key step in the proposed mechanism of phosphine substitution.[4]

The reaction of molecular hydrogen with metal–carbene complexes at high temperature or upon photolysis at room temperature leads to the hydrogenolysis of the carbene ligand.[5] The mechanism proposed for hydrogenation involves initial CO dissociation followed by oxidative addition of hydrogen to the coordinatively unsaturated intermediate.

Arylmethoxycarbene complexes 3 react with α,β-unsaturated esters at 90–140 °C to give cyclopropanes.[6] $(CO)_5WC(C_6H_5)_2$, 4, reacts with alkenes below 50 °C to give cyclopropanes and olefin metathesis-like alkene scission products.[7] These reactions of carbene complexes with alkenes have been proposed to proceed via CO dissociation and reaction of the coordinatively unsaturated intermediate to give a metal–carbene–alkene complex.



In the autocatalytic decomposition of metal–carbene complex 5 an intermediate chelated tungsten–carbene–alkene complex 6 was observed spectrally.[8] The initiation



of the autocatalytic process was proposed to involve CO dissociation from the metal–carbene complex.

The possibility that some of these reactions might take place by direct reactions of coordinatively *saturated* metal–carbene complexes should also be considered. For example, the reaction of phosphines with carbene complexes might involve rearrangement of the zwitterionic intermediate 2. The reaction of vinyl ethers with carbene complexes occurs under such mild conditions[9] that the reaction has been suggested to proceed by attack of the vinyl ether at the carbene carbon of the coordinatively saturated carbene complex.[10] Similarly, the reactions of $(CO)_5WCHC_6H_5$ with alkenes were best explained by direct electrophilic attack of the carbene carbon on the alkene.[11]

Here we report studies of the ^{13}CO exchange reactions of metal–carbene complexes which were designed in part to determine the temperatures required to generate coordinatively unsaturated metal–carbene complexes by CO dissociation. Coordinatively unsaturated carbene complexes can be considered as kinetically competent intermediates only if the ^{13}CO exchange reaction is at least as fast as the reaction in question.

^{13}CO exchange studies also give information about the stereochemistry of ligand exchange. The ^{13}CO exchange studies give direct information about the site preference for CO entry into a 5-coordinate intermediate. The principle of microscopic reversibility requires that the stereochemistry of ligand capture by the 5-coordinate intermediate be identical with the stereochemical preference for loss of CO from the 6-coordinate starting material. The cis:trans selectivity of ligand exchange is of interest since reactions with alkenes presumably require a cis relationship of the carbene and the alkene ligands. Similarly hydrogenolysis and carbene dimer formation should occur via addition of new ligands cis to the carbene ligand.

The ^{13}CO exchange reactions reported here also provide information about the conformational mobility of the 5-coordinate intermediates. For an exchange reaction that exhibits a high initial cis:trans ratio, it is possible to determine whether the 5-coordinate intermediate is fluxional or rigid by monitoring the cis:trans ratio as a function of the extent of exchange. If the reaction is cis selective and

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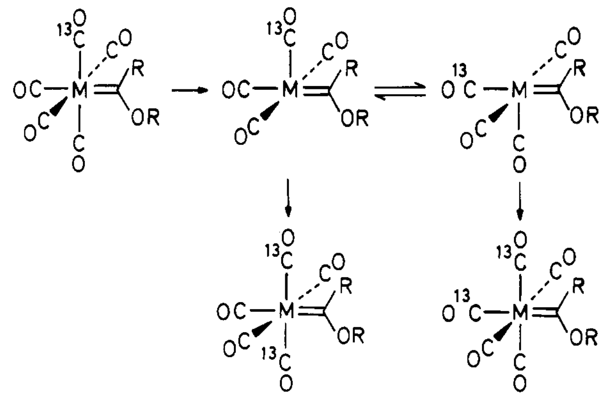
Scheme I



proceeds via a rigid intermediate, the cis:trans ^{13}CO ratio should rise steadily as a function of the extent of exchange. However, if the 5-coordinate intermediate can isomerize, then the cis:trans ^{13}CO ratio would initially rise and then drop significantly as a function of the extent of exchange. This drop in the cis:trans ^{13}CO ratio is due to rearrangement of a cis ^{13}CO ligand to a trans position in the 5-coordinate intermediate and will be important only for molecules undergoing multiple CO exchange. This pathway (see Scheme I) provides a route to trans labeled material even if CO dissociation and recombination are totally cis specific.

Infrared analysis which has been used in related studies of $(CO)_5Re-Br$ by Brown[12] was not capable of giving accurate enough results for our studies of carbene complexes since there is extensive overlapping of CO stretching bands in the IR of $(CO)_5M{=}CRR'$ compounds. Instead, we chose ^{13}C NMR to study the rate and stereochemistry of ^{13}CO exchange with carbene complexes. Direct observation of cis and trans ^{13}CO resonances is straightforward by ^{13}C NMR, but great care must be taken to obtain reliable integrations.[13]

Experimental Section

$(CO)_5Cr{=}C(OCH_3)C_6H_5$[14] (**3Cr**), $(CO)_5W{=}C(OCH_3)C_6H_5$[15] (**3W**), and $(CO)_5W{=}C(C_6H_5)_2$[16] (**4**) were prepared as reported.

Pentacarbonyl(1-oxa-3,3-dimethylcyclopent-2-ylidene)chromium(0) (7). *n*-BuLi in hexane (1.46 M, 5.22 mL, 7.62 mmol) was added to a clear yellow solution of $(CO)_5Cr{=}\overline{C(CH_2)_3O}$[17] (1) (2.0 g, 7.62 mmol) in 100 mL of ether at −78 °C. The resulting milky white suspension was stirred at −78 °C for 10 min, and CH_3OSO_2F (97%, 635 μL, 897 mg, 7.62 mmol) was added. The mixture was stirred at 0 °C for 1 h and cooled to −78 °C before *n*-BuLi (7.62 mmol) was added. After 30 min at −78 °C, CH_3OSO_2F (7.62 mmol) was added and the mixture stirred at 0 °C for 1 h. Aqueous workup followed by column chromatography (silica gel/pentane) gave $(CO)_5Cr{=}\overline{CC(CH_3)_2CH_2CH_2O}$ (7) as bright yellow crystals (1.95 g, 88%): mp 61–62 °C; ^{1}H NMR ($CDCl_3$) δ 4.85 (t, J = 7 Hz, 2 H), 1.78 (t, J = 7 Hz, 2 H), 1.36 (s, 6 H); IR (heptane) 2067 (s), 1982 (m), 1953 (s), 1947 (s), 1930 (s) cm^{-1}.

$(CO)_5Mo{=}C(OCH_3)C_6H_5$ (3Mo) was prepared by the same method used for **3W**.[15] Reaction of phenyllithium (12.4 mmol) with a suspension of $Mo(CO)_6$ (2.64 g, 10 mmol) in ether followed by evaporation of solvent and methylation with $(CH_3)_3O^+BF_4^-$ (1.48 g, 10.0 mmol) in aqueous solution led to the formation of **3Mo**. Column chromatography (silica gel/hexane) and recrystallization from 2 mL of hexane at −22 °C led to the isolation of deep red crystalline **3Mo** (2.0 g, 56%): mp 37–38 °C; ^{1}H NMR (acetone-d_6) δ 7.7–7.2 (m, 5 H), 4.86 (s, 3 H); IR (heptane) 2068 (m), 1988 (w), 1960 (s), 1948 (s) cm^{-1}. **3Mo** was stored under N_2 at −22 °C since it is somewhat less stable than **3Cr** and **3W**.[18–20]

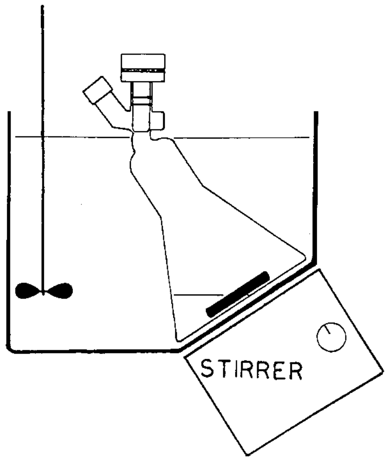


Figure 1. Apparatus for ^{13}CO exchange studies.

^{13}CO Exchange Experiments. The exchange experiments were carried out in a 250-mL Erlenmeyer flask containing a 1.5-in. Teflon-coated magnetic stirring bar and fitted with a 10-mm Teflon O-ring stopcock between the flask and a 14/20 female joint (Figure 1). Solutions of the carbene complexes (0.9–2.0 mmol) in 10 mL of either toluene or *n*-hexane were added to the flask under N_2. The flask was evacuated and then charged with ~ 740-mm 90% ^{13}CO (Mound Laboratory) by using a low volume gas inlet–manometer system that allowed pressure to be measured to ±0.2 mm.

Efficient gas–liquid equilibration was crucial and was achieved by tilting the bottom of the flask to a 30° angle and stirring rapidly. Vigorous splashing and swirling of the solution resulted. A constant temperature bath (±1 °C) was constructed with a flat section of its base at a 30° angle to facilitate the stirring arrangement. A magnetic stirring motor was held against this face of the bath, and the reaction flask was positioned in the oil bath so that it was immersed in the oil bath up to the stopcock with its base parallel to the stirring motor.

To obtain samples, we rapidly transferred the flask to a −10 °C bath to bring the pressure below 1 atm before aliquots (2 mL) were withdrawn from the flask by inserting a long syringe needle through the septum attached to the joint and through the opening created by withdrawing the Teflon plug of the O-ring stopcock. The experiment was resumed by closing the stopcock and replacing the flask in the constant temperature bath. Temperature reequilibration of the solution was achieved within 1 min; the intervals between aliquots were >20 min.

In the cases of the less reactive carbene complexes **7** (0.15 M) and **3W** (0.20 M), exchange reactions were carried out at 77 °C in toluene, and aliquots were purified by passage through a short silica gel column. ^{13}C NMR spectra were taken on a JEOL FX-60 spectrometer at 32 °C.

In the cases of the more reactive compounds, exchange reactions were carried out in hexane at lower temperatures: **3Cr** (44 °C; 0.2 M); **3Mo** (27 °C, 0.15 M); **4** (40 °C; 0.08 M). Hexane was removed from aliquots under vacuum at −10 °C, and ^{13}C NMR spectra were run on a Varian XL-100 spectrometer at low temperature: **3Cr**, 0 °C; **3Mo**, −3 °C; **4**, −23 °C.

^{13}C NMR Analysis. Incorporation of ^{13}CO into the cis and trans sites of the carbene complexes was monitored quantitatively

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[17] Casey, C. P.; Anderson, R. L.; Neumann, S. M.; Scheck, D. M. *Inorg. Synth.* **1979**, *19*, 178.

[18] In 1967, Fischer described **3Mo** as an orange-red crystalline compound which underwent rapid decomposition, and consequently spectral data were not reported.[19] Subsequently, **3Mo** has been used without mention of spectral characterization.[6,20]

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Table I. ^{13}C NMR Spectra of Metal-Carbene Complexes

	signals used in exchange reaction analysis					signals not used in analysis	
			aryl				
compd, solvent	trans CO	cis CO	ipso	para	ortho, meta	$-OCH_3$	carbene
3Cr, CD_3COCD_3	223.8^a	216.9^a	154.7	131.1	129.2, 123.3	66	351
3Mo, CD_3CN	215.0^b	206.6^b	154.7	132.8	129.1, 126.7	71.1	340.3
3W, CD_3CN	205.1^c	198.2^c	156.3	132.6	129.2, 126.8	70	323
4, CD_3COCD_3	215.3^d	198.4^d	167.2	131.4	128.5, 126.3		358
7, C_6D_6	225.1^e	218.9^e	[85.5 (C-5), 68.9 (C-3), 37.4 (C-4), 26.6 (CH_3)]				354.1

^{a} $J_{^{13}\mathrm{C}_{\mathrm{cis}}-^{13}\mathrm{C}_{\mathrm{trans}}} = 5.2$ Hz. ^{b} $J_{^{13}\mathrm{C}_{\mathrm{cis}}-^{13}\mathrm{C}_{\mathrm{trans}}} = 5.0$ Hz. ^{c} $J_{^{13}\mathrm{C}_{\mathrm{cis}}-^{13}\mathrm{C}_{\mathrm{trans}}} = 2.8$ Hz, $J_{^{183}\mathrm{W}-^{13}\mathrm{C}_{\mathrm{cis}}} = 129$ Hz, $J_{^{183}\mathrm{W}-^{13}\mathrm{C}_{\mathrm{trans}}} = 104.2$ Hz. ^{d} $J_{^{13}\mathrm{C}_{\mathrm{cis}}-^{13}\mathrm{C}_{\mathrm{trans}}} = 2.7$ Hz, $J_{^{183}\mathrm{W}-^{13}\mathrm{C}_{\mathrm{cis}}} = 126.6$ Hz. ^{e} $J_{^{13}\mathrm{C}_{\mathrm{cis}}-^{13}\mathrm{C}_{\mathrm{trans}}} = 5.2$ Hz.

Table II. ^{13}CO Exchange of Metal-Carbene Complexes

compd, temp	time, min	peak areas			% cis ^{13}CO	% trans ^{13}CO	$\frac{\text{cis } ^{13}\text{CO}}{\text{trans } ^{13}\text{CO}}$	% ^{13}CO incorporated
		c	t	$\bar{h}$				
3Cr, 44 °C	0	126	35.0	25 ± 2.5	5.5 ± 0.7	1.5 ± 0.2	3.6 ± 0.5	
	40	188	8.5	5.1 ± 0.6	40.5 ± 6.1	1.8 ± 0.3	22.1 ± 3.6	36.9 ± 6.1
	80	220	11.3	3.1 ± 0.1	78.1 ± 3.2	4.0 ± 0.2	19.5 ± 0.9	76.6 ± 3.2
	100	224	16.0	2.9 ± 0.2	85.0 ± 7.5	6.1 ± 0.5	14.0 ± 1.4	85.5 ± 7.6
3Mo, 27 °C	0	207	52.0	53.0 ± 2.0	4.2 ± 0.2	1.1 ± 0.1	4.0 ± 0.2	
	75	305	23.2	18.2 ± 0.9	18.4 ± 1.2	1.4 ± 0.1	13.1 ± 0.9	14.3 ± 1.2
	135	329	21.1	12.1 ± 0.6	29.9 ± 1.9	1.9 ± 0.1	15.6 ± 1.1	26.3 ± 1.9
	225	342	16.3	6.4 ± 0.6	58.8 ± 7.0	2.8 ± 0.3	21.0 ± 2.8	56.1 ± 7.1
	270	261	11.8	4.4 ± 0.4	65.3 ± 7.6	3.0 ± 0.3	22.1 ± 2.8	62.7 ± 7.6
3W, 77 °C	0	143	36	38 ± 1.4	4.1 ± 0.2	1.0 ± 0.1	4.0 ± 0.2	
	90	488	56	30 ± 1.6	17.9 ± 1.2	2.0 ± 0.1	8.7 ± 0.7	14.4 ± 1.2
	180	476	52	22.6 ± 1.6	23.1 ± 2.1	2.5 ± 0.2	9.2 ± 0.9	20.2 ± 2.1
	270	572	61	18.1 ± 0.9	34.8 ± 2.2	3.7 ± 0.2	9.4 ± 0.7	33.0 ± 2.2
	360	696	72	16.6 ± 0.9	46.1 ± 3.2	4.8 ± 0.3	9.7 ± 0.7	45.4 ± 3.2
	450	672	75	11.5 ± 0.9	64.2 ± 6.5	7.2 ± 0.7	9.0 ± 1.0	66.0 ± 6.5
4, 40 °C	0	387	94	95 ± 2	4.5 ± 0.1	1.1 ± 0.1	4.1 ± 0.1	
	120	183	47	7.9 ± 1.0	25.5 ± 4.1	6.5 ± 1.0	3.9 ± 0.7	26.5 ± 4.3
	240	217	50	4.4 ± 0.7	54.2 ± 11.1	12.5 ± 2.6	4.3 ± 1.0	61.2 ± 11.4
	360	285	72	4.0 ± 0.6	78.4 ± 15.1	19.8 ± 3.8	4.0 ± 0.8	92.7 ± 15.5
7, 77 °C	0	284	72	69.1 ± 5.6	4.5 ± 0.5	1.1 ± 0.1	3.9 ± 0.5	
	120	254	32	17.6 ± 1.1	16.0 ± 1.3	2.0 ± 0.2	7.9 ± 0.7	12.5 ± 1.3
	240	242	29	11.6 ± 0.4	22.9 ± 1.0	2.8 ± 0.1	8.3 ± 0.4	20.2 ± 1.0
	360	270	32	7.8 ± 0.3	38.1 ± 1.9	4.5 ± 0.2	8.4 ± 0.5	37.1 ± 1.9
	480	310	44	6.8 ± 0.2	50.1 ± 1.9	7.1 ± 0.3	7.0 ± 0.3	51.8 ± 1.9
	720	482	79	9.4 ± 0.7	56.4 ± 5.4	9.2 ± 0.9	6.1 ± 0.6	60.1 ± 5.5

by Fourier transform (FT) ^{13}C NMR spectroscopy. This was accomplished for each sample by comparing the intensities of the carbonyl resonances (measured by planimeter integration) with those of nonexchanging alkyl or aryl resonances as internal standards. In order to obtain accurate integral measurements, 0.09 M Cr(acac)$_3$ "shiftless relaxation reagent"[21] was added to each sample to reduce the carbon T_1 relaxation times and to suppress nuclear Overhauser signal enhancements.[21,22] Also, a reversed gated broad-band ^{1}H decoupling procedure was used in which the decoupler was on during the data acquisition pulse and off between pulses. This decoupling scheme serves to negate nuclear Overhauser enhancements if the time between pulses (pulse delay) is greater than 5 times the longest carbon T_1 relaxation time in the molecule[23] and has been used to follow ^{13}CO exchange in other metal complexes.[24] Typical NMR conditions included a pulse angle of 90° and a pulse delay of 3–8 s. The shortest pulse delay which gave correct integral ratios for all the carbonyl, alkyl, and aryl resonances of the unexchanged complexes was employed. Spectral widths were chosen as narrow as possible to maximize spectral resolution; for this reason, the carbene carbon atom (δ ~350) was not included in the spectral width. The ^{13}C NMR spectra are listed in Table I.

The ^{13}C data for the exchange experiments is detailed in Table II. For each sample, integral measurements of the trans CO (t), cis CO (c), and aryl or alkyl resonances were made. As an internal standard, a mean single carbon intensity, $\bar{h}$, was computed for each sample as the average aryl or alkyl carbon intensity. The standard deviation of $\bar{h}$ was used to determine error limits for all computations, using standard error propagation formulas. The % ^{13}C label in the cis and in the trans positions (including natural abundance) are simply $c/\bar{h} \times 1.1\%$ and $t/\bar{h} \times 1.1\%$. The observed cis/trans ratio (which includes natural abundance) is c/t. The total % ^{13}C incorporated (over natural abundance) is $[(c + t - 5\bar{h})/\bar{h}] \times 1.1\%$.

Results

Exchange Rates. Solutions of a series of transition-metal–carbene complexes in toluene or hexane under ~740-mm 90% ^{13}CO pressure were stirred rapidly in an apparatus designed to achieve good equilibration of CO between the gas phase and solution. The rate of ^{13}CO incorporation was measured by ^{13}C NMR analysis of aliquots taken from the reactor by comparing the integral measurements for the cis and trans ^{13}CO resonances with those of aryl or alkyl resonances of the carbene ligands. Since temperature was controlled to only ±1 °C and since the reaction mixtures were cooled and reheated during the

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Table III. Rates of CO Dissociation from $(CO)_5M{=}CRR'$

compd	temp, °C	rate,[a] $s^{-1} \times 10^5$	$\Delta G^{\ddagger}$, kcal mol^{-1}
3Cr	44[b]	18.0	24.0
3Mo	27[b]	4.9	23.4
3W	77[c]	2.3	28.0
4	40[b]	4.9	24.5
7	77[c]	1.1	28.5

[a] Rate data are accurate to about ±20%. [b] Hexane solvent. [c] Toluene solvent.

process of taking aliquots, the rates of CO dissociation listed in Table III are accurate to only ±20%. The rates of CO dissociation are corrected for use of 90% ^{13}CO and are 1.11 times greater than the measured rate of ^{13}CO incorporation. These rate data are accurate enough to determine whether a coordinatively unsaturated metal carbene complex $(CO)_4M{=}CRR'$ needs to be considered as a viable intermediate in the reactions of the parent metal–carbene complex $(CO)_5M{=}CRR'$.

Stereochemistry of ^{13}CO Exchange. All of the metal-carbene complexes studied with the exception of $(CO)_5WC(C_6H_5)_2$ showed moderate to high selectivities for the incorporation of ^{13}CO into cis positions. The principle of microscopic reversibility requires that the loss of CO from the metal–carbene complexes also be cis specific. It was not possible to obtain good estimates of the stereospecificity of CO exchange at low levels of incorporation of ^{13}CO. This was primarily due to the difficulty in estimating the small increase over the 1.1% natural abundance of ^{13}CO at the trans position. For example, when **3Mo** was stirred with ^{13}CO for 75 min at 27 °C, the reisolated **3Mo** had 14.0 ± 1.2% above natural abundance ^{13}CO in the cis position and only 0.3 ± 0.1% above natural abundance ^{13}CO in the trans position; the high percentage error in the ^{13}CO in the trans position led to a large error (47 ± 16) in the ratio of ^{13}CO newly incorporated into the cis and trans positions. By measuring the cis:trans ratios at higher ^{13}CO incorporations smaller errors in the % trans ^{13}CO can be achieved, but a new source of uncertainty is introduced. As we pointed out in the introduction, if CO exchange proceeds by a fluxional 5-coordinate intermediate, even if ^{13}CO enters exclusively into cis positions, it is possible to get ^{13}CO into the trans position at longer reaction times. This arises by CO dissociation from *cis*-$(^{13}CO)(CO)_4M{=}CRR'$ to give a fluxional intermediate $(^{13}CO)(CO)_3M{=}CRR'$ which can then give $(^{13}CO)_2(CO)_3M{=}CRR'$ with extensive ^{13}CO in the trans position. Consequently, the observed ratio of cis ^{13}CO:trans ^{13}CO at long reaction times will underestimate the inherent cis stereospecificity of the exchange reaction if the reaction proceeds via a fluxional intermediate.

To circumvent these problems, we have plotted the cis:trans ^{13}CO ratio (without correcting for natural abundance) vs. the total amount of ^{13}CO in the metal–carbene complex. Then kinetic models (Appendix I) involving either a rigid or a fluxional intermediate were employed to try to best fit the data by varying the relative rates of dissociation of CO from a cis or trans site (k_c, k_t). The best estimates of the intrinsic ratio of rates of loss of a cis:trans CO are given in Table IV. Very similar k_c/k_t ratios were obtained with either the rigid or fluxional model for the 5-coordinate intermediate. This is a result of using data primarily from the first 30% ^{13}CO incorporation where the two models give more similar results than they do at more extensive ^{13}CO incorporation.

Conformational Mobility of 5-Coordinate Intermediates. For exchange reactions which display a high cis selectivity, it is possible to distinguish between mechanisms involving a rigid and a rapidly fluxional 5-coordinate intermediate. For reactions involving a rigid intermediate, the cis:trans ^{13}CO ratio rises rapidly from the 4:1 natural abundance ratio as ^{13}CO enters the cis position and continues to rise throughout the incorporation of the first mole of ^{13}CO per mole of carbene complex (Figure 2). For reactions proceeding via a rapidly fluxional 5-coordinate intermediate, the cis:trans ^{13}CO ratio initially rises rapidly from the 4:1 natural abundance ratio as ^{13}CO selectively enters the cis position. However, after about 30% ^{13}CO incorporation the cis:trans ratio peaks and then falls slowly as a second pathway to incorporation of ^{13}CO in the trans position becomes available (Figure 2). This second pathway involves loss of CO from *cis*-$(^{13}CO)(CO)_4M{=}CRR'$ to give *cis*-$(^{13}CO)(CO)_3M{=}CRR'$ which rearranges to give some *trans*-$(^{13}CO)(CO)_3M{=}CRR'$ before capture by ^{13}CO. For reactions proceeding by a fluxional intermediate, about 25% of the doubly ^{13}CO labeled compound will have a trans ^{13}CO label even if ^{13}CO enters only at a cis position.

Table IV. Stereoselectivity of ^{13}CO Exchange into $(CO)_5M{=}CRR'$

compd	cis ^{13}CO/ trans ^{13}CO	stereoselectivity,[a] k_c/k_t
3Cr	>24	>6
3Mo	>36	>9
3W	18 ± 5	4.5 ± 1.2
4	4.0 ± 1.0	1.0 ± 0.25
7	15 ± 4	3.7 ± 1

[a] k_c, k_t are per-site rates.

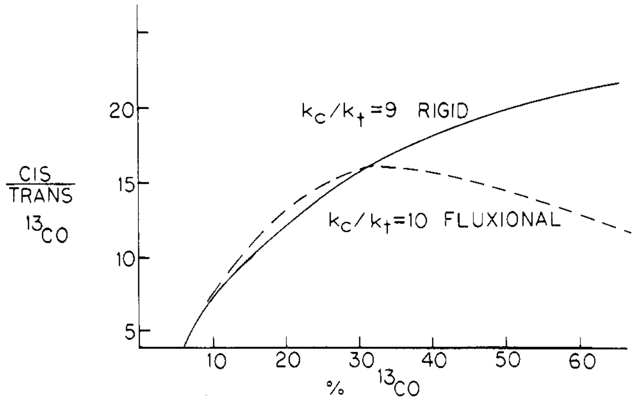

Figure 2. Ratio of cis:trans ^{13}CO vs. % ^{13}CO incorporation. Different ratios of k_c/k_t are shown for the rigid mechanism (k_c/k_t = 9) and for the fluxional mechanism (k_c/k_t = 10) so that the lines are not obscured at low % ^{13}CO incorporation.

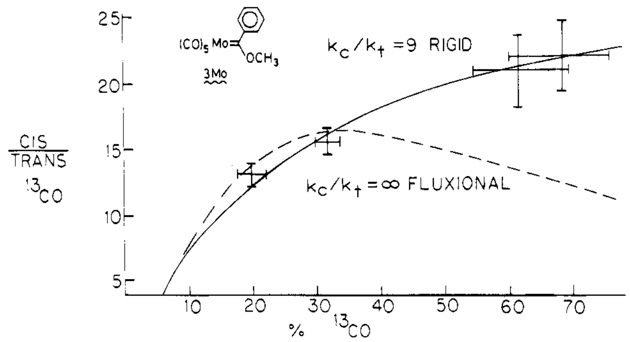

Figure 3. Ratio of cis:trans ^{13}CO vs. % ^{13}CO incorporation for **3Mo**. The theoretical curves for a rigid mechanism with k_c/k_t = 9 and for a fluxional mechanism with k_c/k_t = ∞ are also shown.

The position of the ^{13}CO label in **3Mo** as a function of % ^{13}CO incorporation is shown in Figure 3. It can clearly be seen that the cis:trans ^{13}CO ratio rises continuously to beyond 60% ^{13}CO incorporation. The data are well fitted

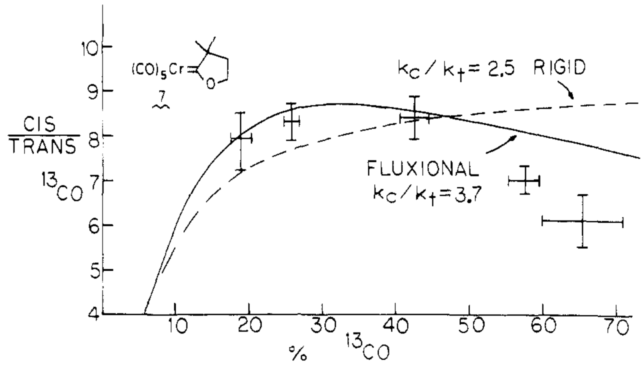

Figure 4. Ratio of cis:trans ^{13}CO vs. % ^{13}CO incorporated for 7. The theoretical curves for a rigid mechanism with $k_c/k_t = 2.5$ and for a fluxional mechanism with $k_c/k_t = 3.7$ are also shown.

to a kinetic model with a rigid intermediate and k_c:k_t = 9. However, the fluxional model cannot fit the data. In particular the fluxional model cannot explain the high cis:trans ^{13}CO ratio at 60–70% ^{13}CO incorporation even if an infinitely high k_c:k_t ratio is chosen.

For 7, the cis:trans ^{13}CO ratio reaches a maximum at about 30% ^{13}CO incorporation and then falls (Figure 4). A better fit to the data can be obtained if the 5-coordinate intermediate is assumed to be fluxional.

For **3Cr** and **3W**, the data can be fit equally well with either a fluxional or rigid model. For 4, the exchange of ^{13}CO was found to be nonstereospecific; consequently, no distinction can be made between a fluxional and a rigid intermediate by this method.

Discussion

Structural Effects on Exchange Rates. The exchange of ^{13}CO with all of the metal–carbene complexes studied here followed first-order kinetics, in agreement with an expected simple CO dissociation mechanism. For the phenylmethoxycarbene complexes, the rate of ^{13}CO exchange of the tungsten complex **3W** ($\Delta G^{\ddagger} = 28.0$ kcal mol^{-1}) was much slower than that of either the molybdenum complex **3Mo** ($\Delta G^{\ddagger} = 23.4$ kcal mol^{-1}) or the chromium complex **3Cr** ($\Delta G^{\ddagger} = 24.0$ kcal mol^{-1}). For the corresponding $M(CO)_6$ compounds, the rates of CO dissociation as measured by $P(C_6H_5)_3$[25] and $P(n\text{-}Bu)_3$[26] substitution reactions are all much slower than for the phenylmethoxycarbene complexes. The same general trend of reactivity Mo > Cr > W is observed in both series of compounds, but the difference in reactivity between **3Mo** and **3Cr** is much smaller than between $Mo(CO)_6$ ($E_a = 31.4$ kcal mol^{-1}) and $Cr(CO)_6$ ($E_a = 38.7$ kcal mol^{-1}).

The ^{13}CO exchange rate of the cyclic alkylalkoxycarbene chromium complex 7 ($\Delta G^{\ddagger} = 28.5$ kcal mol^{-1}) is much slower than that of the phenylmethoxycarbene complex **3Cr** ($\Delta G^{\ddagger} = 24.0$ kcal mol^{-1}).[27] The diphenylcarbene complex of tungsten 4 ($\Delta G^{\ddagger} = 24.5$ kcal mol^{-1}) exchanges ^{13}CO much faster than the phenylmethoxycarbene complex **3W** ($\Delta G^{\ddagger} = 28.0$ kcal mol^{-1}). Both of these reactivity patterns can be explained in terms of the electron donor abilities of the groups attached to the carbene carbon atom. With good electron donor groups attached to the carbene carbon atom there is less demand for donation of π electrons from the metal to the carbene carbon. Consequently the metal is more capable of donating π electrons to the CO ligands and has stronger bonding to CO. The alkyl group in 7 is a better electron donor than the phenyl group in **3Cr**; this results in the observed slower CO dissociation from 7.[28] Similarly, a phenyl group of the diphenylcarbene tungsten complex 4 is a weak electron donor compared with the methoxy group in **3W**, which is a strong π-electron donor to the carbene carbon atom. Consequently, dissociation of a W–CO bond in **3W** is more difficult than in 4.

Comparison of Exchange Rates with Reaction Rates. One motivation for studying the rates of ^{13}CO exchange of metal–carbene complexes was to compare these rates with the rates of various reactions of metal–carbene complexes in order to determine whether a coordinatively unsaturated metal–carbene complex was a kinetically competent intermediate.

The rate of exchange of ^{13}CO with **3Cr** ((1.8 ± 0.5) × 10^{-4} s^{-1} at 44 °C) is within experimental error of the first-order rate constants for the substitution of $P(C_6H_{11})_3$ or of $P(C_6H_5)(CH_2CH_3)_2$ with **3Cr** ((2.6 ± 0.2) × 10^{-4} at 44.5 °C).[27] Thus although **3Cr** and phosphines are in reversible equilibrium with a zwitterionic adduct, the adduct is not involved in the substitution reactions.[29] The slow step in both ^{13}CO exchange and PR_3 substitution is CO dissociation.

Higher temperatures were required for the hydrogenolysis reactions[5] of **3W**, 4, and 7 than for the corresponding ^{13}CO exchange reactions. These observations are in agreement with the proposal that the slow step in the hydrogenolysis reactions is the addition of H_2 to a coordinatively unsaturated metal–carbene complex.

The reaction of metal–carbene complexes with alkenes leads to the formation of cyclopropanes and of olefin metathesis-like alkene scission products. Both of these reactions could proceed via CO dissociation to give a coordinatively unsaturated metal carbene complex which then reacts with an alkene to give a metal–carbene–alkene complex or a metallacyclobutane. Arylmethoxycarbene complexes react with α,β-unsaturated esters at 90–140 °C over 2–6 h to give cyclopropanes.[6] Under these reaction conditions, the ^{13}CO exchange rates of **3Cr**, **3Mo**, and **3W** are all substantially faster than cyclopropane formation. Consequently, a 5-coordinate metal–carbene complex is a reasonable intermediate in these reactions.

Ethyl vinyl ether reacts with **3Cr** at 30 °C over 3 h to give mainly the alkene scission product α-methoxystyrene.[9] However, under 100 atm of CO, a mixture of cyclopropanes is produced. At 44 °C, we have found that the half-life for ^{13}CO exchange of **3Cr** is about 1 h. These results are consistent with formation of a coordinatively unsaturated metal–carbene complex which reacts with ethyl vinyl ether to give successively a metal–carbene–alkene complex, a metallacyclobutane, and eventually α-methoxystyrene. Under CO pressure, the coordinatively unsaturated carbene complex adds CO to revert to **3Cr**; a slower reaction initiated by nucleophilic attack of the vinyl ether on the electron-deficient carbene carbon atom of coordinatively saturated **3Cr** leads to cyclopropane formation. We have proposed a similar mechanism for cyclopropane formation for the reaction of $(CO)_5W{=}CHC_6H_5$ with alkenes at −78 °C where CO dissociation is highly unlikely.[11]

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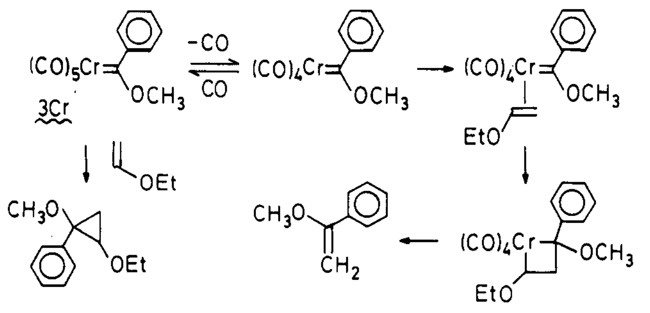
[26] Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082.

[27] Similarly, $(CO)_5Cr{=}C(OCH_3)CH_3$ is 50 times more reactive than $(CO)_5Cr{=}C(OCH_3)C_6H_5$ in ligand-substitution reactions with $P(C_6H_5)(CH_2CH_3)_2$. Werner, H.; Rascher, H. *Helv. Chim. Acta* **1968**, *51*, 1765.

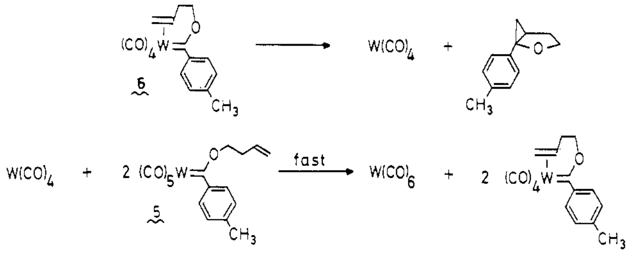
[28] Fischer has studied the infrared spectra of $(CO)_5Cr{=}C(OCH_3)C_6H_4X$ and found that electron-donor substituents lead to decreased CO stretching frequencies and presumably stronger M–CO bonds. Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

[29] The demonstrated first-order kinetics of the phosphine substitution reaction and the independence of the first-order rate constant on the phosphine concentration also establish this fact.[27]



The reaction of diphenylcarbene-tungsten complex **4** with isobutylene at 50 °C for 6 h gave a mixture of alkene scission product diphenylethylene and 2,2-dimethyl-1,1-diphenylcyclopropane.[7] The formation of these products is substantially slower than the rate of CO dissociation from **4** ($t_{1/2}$ = 23 min at 40 °C). The ratio of alkene scission products to cyclopropanes formed in the reaction of 1-pentene with $(CO)_5W{=}C(C_6H_4CH_3)_2$ was found to be independent of CO pressure.[30] These results are in agreement with a mechanism involving CO dissociation, coordination of an alkene, and partitioning of $(CO)_4$(alkene)-$W{=}C(C_6H_5)_2$ between cyclopropane and alkene scission products.

A chelated tungsten-carbene-alkene complex (**6**) was observed as an intermediate in the conversion of carbene complex **5** to cyclopropane. After a 20-min induction period at 38 °C, the decomposition of **5** proceeds rapidly to completion within an additional 20 min.[8] The rate of CO dissociation from the closely related compound **3W** has a half-life of 8.3 h at 77 °C. Consequently, simple CO dissociation from **5** would be much too slow to account for cyclopropane formation. We have proposed a chain mechanism for the autocatalytic decomposition of **5** in which the metal-carbene-alkene complex **6** reacts to give cyclopropane and $W(CO)_4$. The highly reactive $W(CO)_4$ would then react in turn with two molecules of starting material **5** to abstract CO and give rise to 2 equiv of metal-carbene-alkene complex. The dissociation of CO from **5** at 38 °C would be fast enough to be an initiation step to generate the initial metal-carbene-alkene complex.



Stereochemistry of ^{13}CO Exchange. The alkoxy-substituted carbene complexes **3Cr**, **3Mo**, **3W**, and **7** showed moderate to high selectivities for incorporation of ^{13}CO into a cis position. The reactions of metal-carbene complexes with phosphines also lead to kinetically favored cis substitution products.[4,27] The availability of a reactive site cis to the carbene ligand is crucial in the reactions of metal-carbene complexes with hydrogen and with alkenes.

Alkoxy-substituted carbene ligands have a *single* π-acceptor orbital which is a better π-acceptor orbital than either of the *two* π-acceptor orbitals of CO.[31] The CO ligand is a better π-acceptor ligand than a carbene ligand only because it can accept electron density into two different π orbitals. The more rapid dissociation of a cis CO ligand in the alkoxy-substituted carbene complexes is probably related to the stronger σ-donor and weaker π-acceptor ability of the carbene ligand which selectively strengthens the metal-CO bond of the trans CO. The strong σ-donor and weak π-acceptor nature of the carbene ligand also results in a smaller C=O stretching force constant for the trans CO compared to the cis CO ligand.[28,32] While these arguments can explain the relative rates of loss of cis and trans CO ligands, they cannot account for the net labilizing effect of the carbene ligand since the same arguments would lead to the conclusion that loss of CO from $M(CO)_6$ should be favored over loss from $(CO)_5M{=}C(OR)R$.

Lichtenberger and Brown have made an extensive molecular orbital investigation of CO dissociation from $Mn(CO)_6^+$ and $Mn(CO)_5Br$ in an effort to explain the phenomenon of cis labilization of CO dissociation.[33] They concluded that interaction of CO groups with the remainder of the starting complex cannot explain relative rates of CO dissociation. The relative energies of CO dissociation were found to be related to the relative energies of stabilization resulting from geometrical relaxation of the 5-coordinate metal carbonyl fragment formed upon CO loss. Heteroligands with at least one π-donor orbital labilize a cis CO group relative to a trans CO group by providing greater stabilization to the relaxed 5-coordinate intermediate. The precise mode of cis labilization of CO by an alkoxy-substituted carbene ligand is not known, but it can be noted that the carbene ligand is a weaker π-acceptor ligand than CO.[31]

The statistical incorporation of ^{13}CO into $(CO)_5W{=}C(C_6H_5)_2$ (**4**) is surprising since all of the alkoxy-substituted carbene complexes exhibited selective incorporation of ^{13}CO into cis positions. The statistical incorporation of ^{13}CO into **4** might be due to rapid intramolecular isomerization of **4** which would scramble ^{13}CO between cis and trans sites. The intramolecular rearrangement of CO ligands in $(CO)_5WP(OCH_3)_3$ has been reported by Darensbourg.[34]

Fluxional or Rigid 5-Coordinate Intermediates. Plots of the cis:trans ^{13}CO ratio vs. % ^{13}CO incorporation established that the tetracarbonylmolybdenum-carbene intermediate formed from **3Mo** was configurationally rigid; that is, the rate of its reaction with ^{13}CO was faster than its rate of rearrangement. In contrast, the intermediate formed from chromium complex **7** was fluxional. For **3Cr** and **3W**, the data could be fit assuming either a rigid or a fluxional intermediate.

The observation of a rigid intermediate in the reactions of **3Mo** is somewhat unusual in that examples of rigid 5-coordinate d^6 metal complexes are rare but include several molybdenum species such as $(CO)_4Mo$(alkene)[35] and $Mo(CO)_4PR_3$[35] in which the vacant site is cis to the heteroligand. Flood has recently obtained evidence for a rigid, square-pyramidal intermediate in the carbonylation of $(CO)_5MnCH_3$ in THF.[36] Fluxional 5-coordinate d^6 intermediates are more common and include $Mn(CO)_4Br$,[12] $Re(CO)_4Br$,[12] $Cr(CO)_5$,[37] $Mo(CO)_5$,[38] $(phen)Cr(CO)_3$,[39]

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$W(CO)_4$(alkene),[40] and $Mo(CO)_4P(C_6H_5)_3$ (vacant site trans to phosphine).[41]

In the series of metal–carbene complexes studied here, examples of both rigid and fluxional intermediates have been seen. It is likely that the relative rates of rearrangement and of CO capture of the 5-coordinate intermediate are similar in all the cases studied. In some cases, rearrangement is faster than CO capture, and the intermediate is called "fluxional". In other cases, CO capture is more rapid and the intermediate is called "rigid". The rate of capture of 5-coordinate intermediates by ligands has been measured to be between 3×10^6 and 2×10^8 M^{-1} s^{-1}.[42,43] Under the conditions used here (1 atm ≡ 0.01 M CO), the lifetime of the 5-coordinate intermediate before CO capture can be estimated to be between 3×10^{-5} and 5×10^{-7} s. The lifetime before rearrangement is probably also within an order of magnitude of these values.

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged.

Registry No. 3Cr, 27436-93-7; **3Mo**, 38797-47-6; **3W**, 37823-96-4; **4**, 50276-12-5; **7**, 54040-18-5.

Supplementary Material Available: An appendix describing kinetic models and listing differential equations for the rigid mechanism and the fluxional mechanism (9 pages). Ordering information is given on any current masthead page.

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An X-ray Photoelectron Spectroscopic Study of σ- and π-Allyl Groups

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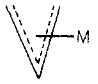
Received June 29, 1981

From a comparison of the atomic core binding energies of $CH_3Mn(CO)_5$, (n-C_3H_7)$Mn(CO)_5$, (σ-C_3H_5)$Mn(CO)_5$, and $Mn_2(CO)_{10}$, we conclude that the methyl, propyl and σ-allyl groups in the first three compounds are negatively charged. Both the carbon 1s binding energies and theoretical considerations indicate an unusually large relaxation energy associated with the ionization of the terminal carbon atom of the σ-allyl group. The π-C_3H_5 group in (π-C_3H_5)$Mn(CO)_5$ has a relatively low electron density, undoubtedly because it is a formal 3-electron donor group. The carbon 1s data indicate that the C_5H_5 group in (η^5-C_5H_5)$Mn(CO)_5$ is probably positively charged.

The allyl group is a commonly encountered ligand in organometallic reactions[1] and catalytic processes.[2] The ligand is of particular interest because it can engage in either η^1 or η^3 bonding to a transition metal; that is, it can be either σ bonded, CH_2═CH-CH_2—M, or π bonded.



In this gas-phase X-ray photoelectron spectroscopic (XPS) investigation we have studied the nature of the bonding of the σ-allyl and π-allyl groups to manganese by comparing the core binding energies of (σ-C_3H_5)$Mn(CO)_5$ and (π-C_3H_5)$Mn(CO)_4$ with those of $CH_3Mn(CO)_5$, (n-C_3H_7)$Mn(CO)_5$, $Mn_2(CO)_{10}$, and (η^5-C_5H_5)$Mn(CO)_3$. In a previous study of a wide variety of $LMn(CO)_5$ compounds, we observed that the manganese, carbonyl carbon, and oxygen core binding energies are linearly correlated with one another.[3] Although the electronegativities and polarizabilities of the L group studied varied over a considerable range, the electronegativities of the L groups were not correlated in any obvious way with the corresponding polarizabilities. If the binding energy shifts were significantly affected by changes in both atomic charge and relaxation energy, one would expect the relative proportions of these changes to be different for the manganese, carbonyl carbon, and oxygen atoms, and therefore that the binding energy shifts would not be linearly related. Hence we believe that those results indicate that the binding energy shifts in such closely related compounds are mainly due to changes in atomic charges and that changes in electronic relaxation energy are relatively small. This conclusion is supported by the general observation that calculated relaxation energies for an atom are similar when the bonding environments of the atom are similar.[4]

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