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Preliminary Communication

Carbonyl Ligand Lability in the μ-$H[Cr(CO)_5]_2^-$ Anion

MARCETTA DARENSBOURG and NYAL WALKER

Department of Chemistry, Tulane University, New Orleans,
Louisiana 70118 (U.S.A.)

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SUMMARY

Studies on the mechanism of the conversion of μ-$H[Cr(CO)_5]_2^-$ to $L_2Cr(CO)_4$ are reported.

X-ray crystal structural analysis of $Et_4N^+\mu$-$H[Cr(CO)_5]_2^-$ [1], in conjunction with nmr coupling constant studies on other VIB metal anions, $MM'H(CO)_{10}^-$ [2], suggested that the hydride ligand acts as a linear bridge between the two octahedral metal centers. To our knowledge this series contains the only verified examples of linear H-bridged dinuclear species. This communication reports on the unexpected lability of the μ-$H[Cr(CO)_5]_2^-$ anion towards carbonyl substitution reactions.

In refluxing absolute EtOH or dry THF, $Et_4N^+\mu$-$H[Cr(CO)_5]_2^-$ may be smoothly converted to trans-$(Ph_3P)_2Cr(CO)_4$ in the presence of even small excesses of PPh_3. With a 10-fold excess of PPh_3, isolated yields of product from EtOH were on the order of 70%, whereas the yields in THF solvent were essentially quantitative. Only the disubstituted product was observed regardless of ligand concentration in the absence of added CO. Furthermore, under the conditions of the studies, $Ph_3PCr(CO)_5$ could not be converted into $(Ph_3P)_2Cr(CO)_4$, neither in the presence of excesses of PPh_3 nor in the presence of PPh_3 and $NaBH_4$. The latter reagent was added to ascertain production of a μ-$H[Cr(CO)_4L]_2^-$ species, similar to the preparation of μ-$H[Cr(CO)_5]_2^-$ from $NaBH_4$ and $Cr(CO)_6$ in THF [2], from an initial product of $Ph_3PCr(CO)_5$.

Rate data obtained by following the disappearance of the ir absorption band due to the most intense CO stretch of μ-$H[Cr(CO)_5]_2^-$ are presented in the Table. For both solvents the reaction obeys first-order kinetics in μ-$H[Cr(CO)_5]_2^-$ and shows essentially no dependence on $[PPh_3]$ at concentrations of PPh_3 to μ-$H[Cr(CO)_5]_2^-$ greater than 10 to 1. At lower PPh_3 concentrations, the rate of disappearance of the carbonyl anion is depressed such that at a 1:1 ratio of ligand to anion the rate is about the same as the decomposition of the anion in the absence of L. Initial studies indicate the reaction rate to be independent of ligand type (expt 12), and a very slight difference in rate was observed in the absence of light (expt 8).

Circulation of N_2 through the reaction solution was found to increase the rate of μ-$H[Cr(CO)_5]_2^-$ decomposition (expt 4), while CO circulation decreased the rate (expts 6 and 7). A separate experiment with ^{13}CO illustrated that labelled CO could be readily incorporated into the anion. Although the broad, overlapped bands prevented quantitative assessment of the relative rates of radial vs. axial CO exchange, the spectra gave clear indication that the initial label incorporation was in the position cis to the hydride bridge [3]. The latter experiment was carried out in the absence of competing PPh_3 ligand and $Cr(CO)_6$ was also observed as product. (At the 1:1 PPh_3 to μ-$H[Cr(CO)_5]_2^-$ ratio, reaction in the presence of CO at 1 atm afforded $Ph_3PCr(CO)_5$ as well as <u>trans</u>-$(Ph_3P)_2Cr(CO)_4$.)

Several lines of evidence, rate behavior that is first-order

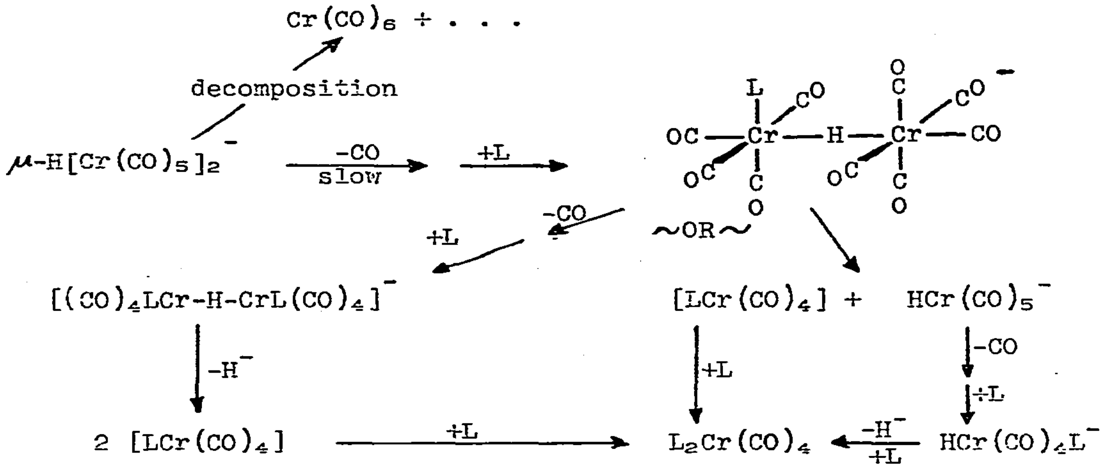
TABLE

KINETIC DATA FOR THE REACTION OF TRIPHENYLPHOSPHINE WITH Et_4N^+ μ-$H[Cr(CO)_5]_2^-$.

Expt.[a]	$[Ph_3P]/[\mu\text{-}H[Cr(CO)_5]_2^-]$	Solvent	Temp (°C)	$k \times 10^4 (sec^{-1})$[b]
1	50	EtOH	78	2.43 (± .01)
2	25	EtOH	78	2.43 (± .01)
3	11.5	EtOH	78	2.50 (± .01)
4	0[c]	EtOH	78	2.11 (± .01)
5	0	EtOH	78	1.72 (± .01)
6	0[d]	EtOH	78	1.25 (± .01)
7	13[d]	EtOH	78	2.09 (± .02)
8	11[e]	EtOH	78	2.33 (± .01)
9	12	THF	66	0.31 (± .02)
10	12	THF/diglyme[f]	80	1.33 (± .02)
11	12	THF/HCl[g]	66	3.66 (± .01)
12	30[h]	EtOH	78	2.41 (± .01)

a. Reactions run under constant 1 atm pressure of N_2 over 2 half-lives; $[\mu\text{-}H[Cr(CO)_5]_2^-] = 3.9 \times 10^{-3}$ M.
b. The errors represent standard deviations at the 95% confidence level; reproducibility was within 7%.
c. The solution was swept with N_2 during reflux.
d. Carbon monoxide was circulated through the solution during reflux.
e. Dark reaction.
f. Eight ml diglyme (bis(2-methoxyethyl)ether) and 15 ml THF.
g. The solution was 0.5 M in anhydrous HCl.
h. The ligand was $P(OPh)_3$.

in the hydrido-carbonyl anion, the independence of rate on L concentration at [L]/[anion] >10, the ^{13}CO incorporation, an observed rate depression in a closed system, and a rate enhancement when an inert gas swept the system, all suggest CO dissociation to be involved in the rate-determining step. Furthermore the general failure to observe a $Ph_3PCr(CO)_5$ product (in the absence of large concentrations of CO) suggests that the coordinatively unsaturated $Cr(CO)_5$ <u>is not</u> produced as an important intermediate, if at all. The following set of reactions are formulated so as to be consistent with these points as well as the observed di-substituted product. The positioning of L cis to the hydride bridge is in accordance with the ^{13}CO labeling study, however the possibility of different stereochemical pathways for the CO exchange and the L substitution certainly exists.



The electronic mechanism of the initial CO labilization by the hydride bridge is subject to conjecture. Several modes of reaction are available to M-H bonds and these include the following: i) removal of H· thus producing reactive radical species [4]; ii) carbonyl insertion into the M-H bond to give a reactive formyl intermediate [5]; iii) ground state destabilization of M-CO by -H- via the direct donation process [6]; and iv) transition state stabilization according to Brown's Site Preference model [7]. Due to the ease of data reproducibility both in the absence and presence of light and O_2, the possibility of radical intermediates seem doubtful. Direct donation from the already electron deficient bridge H^- into the π^* orbitals of the CO also seems unlikely. We are presently attempting to reckon with the remaining possibilities.

The Cotton-Kraihanzel [8] equatorial CO force constant of μ-$H[Cr(CO)_5]_2^-$ was computed to be 15.64 mdynes/Å while the axial CO force constant had the extremely low value of 14.32 mdynes/Å. Since lower CO force constants signify smaller CO and greater MC bond orders, the axial CO is expected to be more tightly bound to the Cr as well as to carry more negative charge. This data is consistent with preferential dissociation of the cis carbonyl group and we propose it to also be consistent with the observed solvent effect. (See for example expt 10; the reaction is slower in an aprotic solvent.)

Specific interaction of alkali metal ions (M'^+) with metal carbonyl anions has been observed [9,10] and a general polarization of the anion towards the positive charge results in decreased carbon to oxygen bond order for the carbonyl group O-complexed to the alkali metal ion, e.g., $M{=}C{\equiv}O| \cdots M'^{+}$. In concordance, those carbonyl groups <u>not</u> complexed to M'^{+} show an increased carbonyl force constant [9]. The transition metal-carbon bond strengths are expected to be in the reverse order, i.e., a lowering of the metal-carbon bond order is expected for those groups which do not interact with the alkali-metal ion. This line of reasoning is appropriate to the acid catalysis observed here. The acid proton of HCl in THF (expt 11) or of EtOH could very reasonably promote CO dissociation by specifically interacting with the more negative carbonyl oxygen, $M\overset{..}{-}C\overset{..}{=}O|\cdots H^+$, thus enhancing the dissociation of the non-interacting CO groups.* The two effects, hydride labilization of CO's cis to the bridge, and positive charge stabilization of the M-C trans to the bridge thus complement each other in promoting cis CO dissociation.

Finally there is an obvious similarity between the μ-$H[Cr(CO)_5]_2^-$ behavior towards ligand substitution and the Chatt, et al. synthesis of $L_2M(CO)_4$ and $L_3M(CO)_3$ using $M(CO)_6$ and L with $NaBH_4$ as catalyst or facilitator[12]. Both reagents, Et_4N^+ μ-$H[Cr(CO)_5]_2^-$ and $Cr(CO)_6/NaBH_4$ (1:10 ratio) react with PPh_3 to produce only trans-$(Ph_3P)_2Cr(CO)_4$ at essentially equal rates. The $Na^+\mu$-$H[Cr(CO)_5]_2^-$ salt is however not readily formed in EtOH, and if indeed it is the intermediate in Chatt's synthesis, small steady-state concentrations only are present. There exists the possibility that the ligand labilizing effect occurs by an initially formed $H{-}\overset{O}{\overset{\|}{C}}{-}Cr(CO)_5^-$ anion, or via a $^-H_3B{-}H{-}Cr(CO)_5^-$ electron deficient bridge system rather than the analogous Cr-H-Cr bridge. Several tetrahydroborato complexes have been reported, for example $RuH(BH_4)(PPh_3)_3$ [13], $RuH(BH_4)CO(PPh_3)_3$ [13], as well as $ML(BH_4)(h^5\text{-}C_5H_5)_2$ ($L = H^-$ or BH_4^-; $M = Zr$ or Hf) [14], however such labilizing ability has not been explored. We have initiated studies in this area.

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*Acid catalysis has previously been reported for the carbonyl exchange reaction of $Fe(CO)_5$ [11]. The proposed scheme for the increased CO lability involved the rapid, reversible formation of the 6-coordinate $HFe(CO)_5^+$, which then lost CO in the rate-determining step. Expansion of the coordination sphere is however unlikely in the Cr complex discussed in this report.

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