

being close to the lower limit usually observed for hydrogen bonding.²⁷ In this manner a linking through hydrogen bonding of complexes related by the *c* glide occurs throughout the unit cell.

One other structural report of a silver(II) complex with a tetradentate nitrogen donor macrocycle has appeared: a (tetraphenylporphyrin)silver-tetraphenylporphyrin molecular solid solution.²⁸ This compound was actually a solid solution of the silver and free base porphyrin with the silver occupying the porphyrinato central hole 54% of the time. The silver and four nitrogens were found to be coplanar with an Ag-N bond length of 2.063 (5) Å. This rather short Ag-N bond length compared to other Ag(II) structures could be an artifact of the disorder but more probably is a consequence of the well-documented propensity of porphyrins to attain a central hole radius of approximately 2.01 Å.²⁹

The [Ag(*meso*-[14]ane)][NO₃]₂ structure is thus the first reported on a silver(II) macrocyclic complex with a completely saturated nitrogen donor ligand. Weak axial coordination also appears to be characteristic of Ag(II) complexes^{17,25,26,30} and is, of course, well documented for Cu(II).³¹ Additional silver complexes in various oxidation states are currently being investigated to elucidate further the influence of macrocyclic ligands on coordination and bonding of the silver ion.

Acknowledgment. I wish to thank Professor Reynold T. Iwamoto for a sample of [Ag(*meso*-[14]ane)][NO₃]₂ and Professor B. K. Lee for use of his x-ray crystallographic program library. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Kansas General Research Fund, for support of this research.

Registry No. [As(*meso*-[14]ane)][NO₃]₂, 64598-79-4.

Supplementary Material Available: Tables II, the structure factor listings, IV, the positional and thermal hydrogen parameters, and V, the interatomic distances involving hydrogens (22 pages). Ordering information is given on any current masthead page.

References and Notes

- J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 315 (1974).
- H. N. Po, *Coord. Chem. Rev.*, **20**, 171 (1976).
- G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Chem. Soc. A*, 1108 (1968).
- D. P. Murtha and R. A. Walton, *Inorg. Chem.*, **12**, 1278 (1973).
- M. O. Kestner and A. L. Allred, *J. Am. Chem. Soc.*, **94**, 7189 (1972).
- E. K. Barefield and M. T. Mocella, *Inorg. Chem.*, **12**, 2829 (1973).
- Computer programs for the unit cell calculations and collection of data were supplied by Syntex Analytical Instruments.
- P2, operations manual.
- G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry", Wiley, New York, N.Y., 1949, p 214.
- P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
- The programs used were local modifications of A. Zalkin's FORDP for the Fourier summation, W. Busing, K. Martin, and H. Levy's ORFLS and ORFFE-II for least-squares and function and error calculations, and C. K. Johnson's ORTEP-II for the molecular structure drawing. Computations were performed on the Honeywell 635 and 66/60 computers at the University of Kansas.
- D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **18**, 104 (1965).
- D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- J. A. Ibers, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, Tables 3.3.1A and 3.3.2C.
- L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969).
- L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 1505 (1973).
- M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc. A*, 1405 (1970).
- N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1408 (1973).
- N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1963 (1973).
- W. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H.-J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974).
- R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, *J. Chem. Soc. A*, 2407 (1969).
- F. Hanic and M. Serator, *Chem. Zvesti.*, **18**, 572 (1964).
- P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).
- H. Ondik and D. Smith, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, Table 4.1.5.
- J. L. Atwood, M. L. Simms, and D. A. Zatko, *Cryst. Struct. Commun.*, **2**, 279 (1973).
- G. W. Bushnell and M. A. Khan, *Can. J. Chem.*, **50**, 315 (1972).
- W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968.
- M. L. Schneider, *J. Chem. Soc., Dalton Trans.*, 1093 (1972).
- J. L. Hoard, *Science*, **174**, 1295 (1974).
- M. G. B. Drew, R. W. Matthews, and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, **6**, 277 (1970).
- P. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972.

Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Ligand Lability Studies in Bridging Hydride Complexes of Group 6B Metal Carbonylates

MARSETTA Y. DARENSBOURG,* NYAL WALKER, and ROBERT R. BURCH, JR.

Received April 26, 1977

The reactions of Et₄N⁺μ-H[M(CO)₅]₂⁻ (M = Cr, Mo, W) with 5A donor ligands have been studied. The predominant if not exclusive product in all cases studied here is L₂M(CO)₄. The reaction follows a rate law that is first order with respect to the concentration of bridging hydride carbonylate and zero order with respect to the 5A donor ligand concentration when the ligand is in a tenfold or greater excess. Rate constants are dependent on metal (Mo > Cr > W) and on solvent (EtOH > THF). It is proposed that initial substitution occurs on the hydride-bridged dimer, prior to dimer disruption. A complex formulated as Et₄N⁺μ-H[Mo(CO)₅][Mo(CO)₄PPh₃]⁻ was isolated as the first-formed product in the Et₄N⁺μ-H[Mo(CO)₅]₂⁻ reaction with PPh₃ in THF. Rates of reaction of μ-H[M(CO)₅]₂⁻ with L to form L₂M(CO)₄ were compared with rates of the nucleophile-facilitated substitution reaction, NaBH₄/M(CO)₆/L, also to form L₂M(CO)₄ or L₃M(CO)₃. The intermediacy of a bridging hydride, μ-H[M(CO)₅]₂⁻, in the sodium borohydride facilitated substitution reactions of M(CO)₆ is consistent with the formation of μ-H[M(CO)₅]₂⁻, reaction rates, and products.

Introduction

The nucleophile-facilitated preparation of group 5A donor ligand substituted 6B metal carbonyls or iron carbonyls has been the subject of several reports recently. This interest stems from a need to develop facile or specific syntheses under mild conditions and has the potential of contributing to the

challenging area of mechanistic information regarding small molecule or ion loss from low-valent metal complexes. Specifically the reports have included the following. Chatt et al. reported the synthesis of a great number of di- and trisubstituted 6B metal carbonyls as "catalyzed" by sodium borohydride, in refluxing EtOH.¹ Shaw and Hui utilized a

phase-transfer process, i.e., $M(\text{CO})_6$ and L in benzene in contact with 50% aqueous NaOH and a small amount of $n\text{-Bu}_4\text{N}^+\text{I}^-$, to prepare $\text{LM}(\text{CO})_5$, $(\text{L-L})\text{M}(\text{CO})_4$, and $\text{L}_2\text{M}(\text{CO})_4$ complexes.² Lithium aluminum hydride was used to facilitate the production of monosubstituted $\text{LFe}(\text{CO})_4$ from $\text{Fe}(\text{CO})_5$ and L in refluxing THF.³ Amine oxides have also been used to enhance carbonyl substitution of $\text{Fe}(\text{CO})_5$ by diolefins yielding $(\text{||-||})\text{Fe}(\text{CO})_3$ in good yields, and rapidly, even at low temperatures.⁴ Trimethylamine oxide has also been successfully used to promote CO loss on clusters such as $\text{Ir}_4(\text{CO})_{12}$, an important step in metal cluster catalysis.⁵ We have observed production of both $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ when $\text{Li}^+\text{Fe}(\text{CO})_4\text{C}(\text{O})\text{Ph}^-$, produced from $\text{Fe}(\text{CO})_5$ and PhLi , is acidified in the presence of L.⁶ In none of the above have complete reaction paths been elucidated.

In the course of investigating the reaction pathway of the sodium borohydride assisted $\text{Cr}(\text{CO})_6$ substitution reactions we reported preliminary results for ligand substitution reactions of a possible intermediate, $\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$.⁷ Similar time periods were required and similar products obtained from the reaction of PPh_3 , for example, with $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$ as in the Chatt synthesis; however, the intermediacy of the bridging hydride in the $\text{NaBH}_4/\text{Cr}(\text{CO})_6/\text{L}$ reaction was not established. This contribution further details the reaction of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ salts with L, defining the reaction dependency on M, solvent, and the nature and concentration of L. Comparisons of such reactions with the studies of nucleophile-assisted substitution reactions are further discussed.

Experimental Section

Materials and Preparations. Tetrahydrofuran was purified by distillation under N_2 from a deep purple solution of 0.1 M Na/benzophenone. Anhydrous ethanol was flushed with N_2 and used without further purification. Tetraethylammonium salts of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ were prepared and purified according to the method of Hayter.⁸ The deuterio derivatives were prepared in an analogous manner using 99% NaBD_4 in the reaction with $\text{M}(\text{CO})_6$ in THF. All preparations were carried out under N_2 . A typical preparation of the compound formulated as a Ph_3P -substituted dinuclear complex salt, $\text{Et}_4\text{N}^+[(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4\text{PPh}_3]^-$, is as follows. A solution containing 80 mL of THF, 0.84 g (1.4 mmol) of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$ and 3.75 g (14 mmol) of PPh_3 was refluxed for 2.25 h, cooled, and filtered. One hundred milliliters of hexane was added to the filtrate, and, upon standing overnight at 5 °C, fine yellow needle-like crystals were isolated and dried under vacuum, yield 0.66 g or 57%. Anal. Calcd for $\text{C}_{35}\text{H}_{36}\text{O}_3\text{Mo}_2\text{NP}$: C, 50.20; H, 4.33; Mo, 22.91; N, 1.67; P, 3.70. Found: C, 50.32, 50.14; H, 4.14, 4.33; N, 1.63, 1.67; Mo, 23.04, 23.12; P, 3.73, 3.75 (Galbraith Laboratories).

Kinetic Measurements. The kinetic studies were carried out in a 50-mL round-bottomed flask, maintained at temperatures sufficient for mild reflux of solvents under a very slight positive pressure of N_2 maintained by a mineral oil outlet. Thus the dry components, $\text{Et}_4\text{N}^+\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ and L, were placed in the flask which was subsequently flushed with N_2 , and the requisite amount of solvent added via syringe. The solution was stirred magnetically and immersed in a preheated oil bath; reflux temperatures were achieved within 3 min. Access to the flask for sampling was via a long syringe needle, through a water-cooled condenser, equipped with an N_2 inlet at its serum-capped top. Samples for IR spectral analysis were withdrawn periodically and placed in a sealed 0.1-mm pathlength NaCl infrared cell. Rates of reaction were observed by following the disappearance of the most intense $\nu(\text{CO})$ absorption of each species investigated. Rate constants were calculated using a linear-least-squares program for the first-order rate plots of $\ln(A_t - A_\infty)$ vs. time, where A_t is the absorbance at time t and A_∞ is the absorbance at time infinity. In the case of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$ reactions, overlapping bands of reactant and the initial product, $\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$, necessitated a correction for changes in baseline absorption. This was effected by obtaining molar absorptivity coefficients of each species at 1928 and 1941 cm^{-1} , their respective band maxima, and solving simultaneous equations for the absorbance due to the reactant.

Spectral Measurements. A Perkin-Elmer 521 grating infrared spectrophotometer, calibrated in the CO stretching region with CO

Table I. Products of the Reaction of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ with L in EtOH and/or THF

$\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ M =	L	Product	Ref
M = Cr	PPh_3	<i>trans</i> - $\text{Cr}(\text{CO})_4\text{L}_2$	9, a
Mo	PPh_3	<i>cis</i> - $\text{Mo}(\text{CO})_4\text{L}_2$ ^b	10
W	PPh_3	<i>trans</i> - $\text{W}(\text{CO})_4\text{L}_2$	11
Cr	$\text{P}(\text{OPh})_3$	<i>cis</i> - $\text{Cr}(\text{CO})_4\text{L}_2$	9
Mo	$\text{P}(\text{OPh})_3$	<i>cis</i> - $\text{Mo}(\text{CO})_4\text{L}_2$	10, a
Cr	PMe_2Ph	<i>cis</i> - $\text{Cr}(\text{CO})_4\text{L}_2$	12
Cr	$\text{P}(\text{OCH}_2)_3\text{C-Et}$	<i>cis</i> - $\text{Cr}(\text{CO})_4\text{L}_2$ ^b	a

^a Alternate route synthesis, this work. ^b Product predominantly (>90%) of *cis* geometry, <10% *trans* by IR analysis.

and H_2O vapor, was used to obtain all frequency and rate data. Proton NMR spectra were run on a JEOLCO C-60 spectrometer.

Results and Discussion

The reactions of tetraethylammonium salts of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ (M = Cr, Mo, W) with various phosphines and phosphites proceeded to give the $\text{L}_2\text{M}(\text{CO})_4$ products in all cases investigated. The geometry of the complexes is predominantly *cis*; however, the *trans* products are observed for L = PPh_3 and M = Cr and W. Yields as determined spectrophotometrically appeared in general to be nearly quantitative; when run on a preparative scale, isolated yields were around 70%. The complete list of reactions investigated and product geometries is given in Table I. Product identification was effected by comparison of $\nu(\text{CO})$ infrared spectra to those of known compounds either from the literature or from an alternate route synthesis.

Although prolonged reaction of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$ with PPh_3 leads to production of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$,¹³ the first-formed product may be formulated as a substituted dinuclear ion, $\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$, according to elemental analysis and the following structural probes. In addition to the ethyl and phenyl resonances, the ^1H NMR shows a doublet centered at 11.10 ppm upfield from Me_4Si which has a $J_{\text{P-H}}$ of 20 Hz. The hydride resonance of $\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$ is a singlet at 12.15 ppm. The ionization of the compound in THF as determined by dependence of conductance on concentration is similar to that of the parent $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$. Attempts to determine detailed assignments of the $\nu(\text{CO})$ IR spectrum were complicated by considerable overlap of bands; however, a most probable symmetry of C_{4v} at one octahedral center and C_{2v} at the other is suggested. (C_{4v} center assignments: $A_1^{(2)}$, 2053 (w); $A_1^{(1)}$, 1890 (m, sh); E, 1928 (s) cm^{-1} (1962 (vw) is assigned to the formally forbidden B_1 mode). (C_{2v} center assignments: $A_1^{(2)}$, 2001 (w); $A_1^{(1)}$, 1915 (m, sh) (estimated); B_1 , 1875 (m); B_2 , 1840 (m) cm^{-1} .) Here, the substituent is believed to be positioned *cis* to the hydride bridge, consistent with the earlier observation of ^{13}C incorporation preferentially *cis* to the hydride bridge in $\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$.^{7,14} Furthermore a precedent for this type of compound is $(\text{CO})_5\text{W-H-W}(\text{CO})_3\text{-P}(\text{OMe})_3(\text{NO})$, which may be prepared by stirring together $(\text{CO})_5\text{W-H-W}(\text{CO})_4\text{NO}$ and $\text{P}(\text{OMe})_3$ in hexane over a period of 40 hours at room temperature.¹⁵ X-ray and neutron diffraction studies have determined the $\text{P}(\text{OMe})_3$ ligand to be bound to the tungsten atom bearing the nitrosyl and *cis* to the hydride bridge. An interesting observation in both of these 5A ligand-substituted binuclear complexes is that the average $\nu(\text{CO})$ in the substituted complexes are to slightly higher frequencies than in the all-carbonyl complexes. A complete list of $\nu(\text{CO})$ frequencies for the bridging hydrides and deuterides used in this study as well as the tungsten nitrosyl hydrides is found in Table II.

Salts of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ are thermally unstable in solution. In the presence of trapping ligands such as phosphines or phosphites the decomposition rate is enhanced.⁷ The disap-

Table II. Carbonyl Stretching Frequencies of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ and Related Compounds

Compd	Solvent	ν , cm^{-1}	Ref
$\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$	THF	2029 w, 1937 s, 1876 m	8, a
$\mu\text{-D}[\text{Cr}(\text{CO})_5]_2^-$	THF	2029 w, 1940 s, 1877 m	a
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	THF	2038 w, 1941 s, 1878 m	8, b
$\mu\text{-D}[\text{Mo}(\text{CO})_5]_2^-$	THF	2039 w, 1941 s, 1876 m	a
$\mu\text{-H}[\text{W}(\text{CO})_5]_2^-$	THF	2039 w, 1936 s, 1875 m	8, a
$(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4\text{PPh}_3^-$	THF	2053 w, 2001 w, 1928 s, 1875 m, 1840 m	a
$(\text{CO})_5\text{W-H-W}(\text{CO})_4\text{NO}$	cyclohexane	2069 m, 2045 s, 2011 w, 1989 w, 1953 sh, 1944 s	16
$(\text{CO})_5\text{W-H-W}(\text{CO})_3(\text{P}(\text{OMe})_3)\text{NO}$	cyclohexane	2095 w, 2060 s, 2017 w, 2003 s, 1966 w, 1915 vs, br	15

^a This work. ^b These frequencies differ from those in ref 8 which report $\nu(\text{CO})$ of 2035 cm^{-1} (w), 1920 (vs), and 1860 (s).

Table III. First-Order Rate Constants for the Disappearance of Et_4N^+ Salts of Hydrido and Deuterio Dinuclear Carbonylates

Carbonylate ^a	Ligand	[L], M	Solvent (reflux)	$10^4 k$, ^b s^{-1}
$\mu\text{-H}[\text{W}(\text{CO})_5]_2^-$	PPh_3	0.037	EtOH	0.314 ± 0.02
$\mu\text{-H}[\text{W}(\text{CO})_5]_2^-$	PPh_3	0.058	THF	0.0435 ± 0.0021
$\mu\text{-H}[\text{W}(\text{CO})_5]_2^-$	PPh_3	0.048	THF (0.3 M HCl)	0.088 ± 0.014
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	PPh_3	0.034	THF	4.54 ± 0.56
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	PPh_3	0.034	THF (dark)	4.70 ± 0.25
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	PPh_3	0.068	THF	4.40 ± 0.48
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	PPh_3	0.102	THF	4.41 ± 0.15
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	PPh_3	0.102	THF (dark)	4.92 ± 0.19
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	PPh_3	0.136	THF	4.80 ± 0.12
$\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	PPh_3	0.170	THF	4.98 ± 0.18
$\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$	PPh_3	$0.041\text{--}0.17^c$	EtOH	2.45 ± 0.10^c
$\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$	PPh_3	0.041	THF	0.31 ± 0.03
$\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$	PPh_3	0.041	THF (0.5 M HCl)	3.66 ± 0.15
$\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$	$\text{P}(\text{O}^i\text{Pr})_3$	$0.10\text{--}0.17$	EtOH	2.37 ± 0.67^c
$\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$	PMe_2Ph	0.048	EtOH	2.88 ± 0.04
$\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$			EtOH	1.72 ± 0.30^d
$\mu\text{-D}[\text{Cr}(\text{CO})_5]_2^-$			EtOH	2.03 ± 0.12^d
$\mu\text{-D}[\text{Cr}(\text{CO})_5]_2^-$	PPh_3	0.041	EtOH	2.70 ± 0.04
$(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4\text{PPh}_3^-$	PPh_3	$0.041\text{--}0.164^e$	THF	$0.253\text{--}0.442$

^a [Carbonylate] = 3.4×10^{-3} M. Reactions run under constant 1 atm of pressure of N_2 over two to three half-lives. ^b Except where noted, k 's are determined for a single kinetic run, utilizing 10–20 individual measurements per run. The uncertainties are expressed at the 95% confidence limit. ^c The value for k is the average of values for several runs in this concentration range. The error is an expression of the 95% confidence limit for replication (and hence are measures of the reproducibility of the rate data), neglecting or not weighing the (small) errors in individual runs. ^d The value for k is the average of three replicate runs, and the error is as discussed in *c*. ^e In this ligand concentration range the value of k is directly dependent on [L].

pearance of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ or $\mu\text{-D}[\text{M}(\text{CO})_5]_2^-$ both in the presence and in the absence of L shows a first-order rate dependence on the concentration of anion. As listed in Table III, the first-order rate constants show definite dependencies on M (Mo > Cr > W) and on solvent (EtOH > THF), and only slight variations with various L groups. Within experimental error the disappearance of the carbonyl anion is independent of PPh_3 concentration, over a range of 12- to 50-fold excess of PPh_3 for M = Cr and Mo. Carbon monoxide, however, effectively competes with PPh_3 , decreasing the rate constant by a significant amount. (Reaction products under these conditions contain some mono- as well as disubstituted products.) The presence of carbon monoxide also retards the decomposition rate in the absence of a 5A donor ligand. The decomposition rate may be enhanced by sweeping the solution with N_2 .⁷ As was the case with the previously reported chromium derivatives, a rate enhancement was observed upon addition of anhydrous HCl to THF solutions of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{W}(\text{CO})_5]_2^-$ and PPh_3 . Addition of a four- to eightfold excess of NaBPh_4 did not influence the rate of decomposition of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$ in THF.

The rate constants for decomposition of the deuteride, $\mu\text{-D}[\text{Cr}(\text{CO})_5]_2^-$, are also given in Table III. There is a slight enhancement of rate constants when compared to the corresponding hydrido reaction; i.e., a small "inverse isotope effect" exists.

Due to the difficulties of band resolution, a substantial error was associated with the Mo kinetic studies as evidenced by large standard deviations and lower reproducibility. In contrast, the Cr and W data were quite consistent and reproducible. Kinetic studies carried out in the dark gave es-

entially the same rate constants as those studies made in the presence of light and gave no greater reproducibility.

The reaction of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$ with PPh_3 to yield *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ follows a first-order rate dependence on the carbonylate concentration but shows some dependence on PPh_3 concentration. As indicated in Table III, k_{obsd} for the disappearance of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$ clearly is much smaller than k_1 for the disappearance of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$ at all [similar] ligand concentrations investigated.

The fact that very little $\text{LM}(\text{CO})_5$ product is observed in these reactions suggests that the disubstituted $\text{L}_2\text{M}(\text{CO})_4$ complexes are formed without benefit of an $\text{LM}(\text{CO})_5$ initial product. This was further checked by monitoring the reaction of $\text{Ph}_3\text{PCr}(\text{CO})_5$ with a tenfold excess of PPh_3 in refluxing EtOH in the presence of a fivefold excess of NaBH_4 and in its absence. There is no rate enhancement of further PPh_3 substitution in $\text{Ph}_3\text{PCr}(\text{CO})_5$ in the presence of NaBH_4 over that in the absence of the latter reagent. Furthermore, the rate of production of *trans*- $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$ under those conditions is much slower than in either the $\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$ or the $\text{NaBH}_4/\text{Cr}(\text{CO})_6$ preparation (see footnote *c* of Table IV).

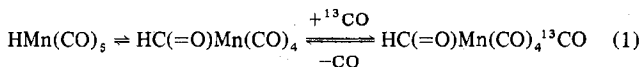
In view of the interest in substitution reactions of binuclear and higher clusters of metal carbonyls, it is appropriate to further define or speculate on the contribution of these data toward problems of that type. Several published works are pertinent to formulation of an overall mechanistic scheme for $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ substitution reactions. Substitution reactions of $\text{HMn}(\text{CO})_5$ by phosphines, arsines, and ^{13}CO have recently been kinetically investigated by Brown and Byers.¹⁷ The

Table IV. Comparison of Reaction Rates and Products of the $M(\text{CO})_6/\text{NaBH}_4/\text{PPh}_3$ Reaction^a and $\text{Et}_4\text{N}^+\mu\text{-H}[\text{M}(\text{CO})_5]_2^-/\text{PPh}_3$ Reaction in Refluxing EtOH under N_2

Reactant	$\text{Ph}_3\text{P}/\text{MCO}$ ratio	$10^4 k, \text{s}^{-1}$	Product
$\text{Cr}(\text{CO})_6 + \text{NaBH}_4$ ^b	5 ^c	1.53 ± 0.04 ^c	<i>trans</i> - (Ph_3P) ₂ $\text{Cr}(\text{CO})_4$
$\text{Et}_4\text{N}^+\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$	12-50	2.45 ± 0.01	<i>trans</i> - (Ph_3P) ₂ $\text{Cr}(\text{CO})_4$
$\text{Mo}(\text{CO})_6 + \text{NaBH}_4$ ^d	14	4.21 ± 0.10 ^e	<i>cis</i> - (Ph_3P) ₂ $\text{Mo}(\text{CO})_4$
$\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$	12	~30	<i>cis</i> - (Ph_3P) ₂ $\text{Mo}(\text{CO})_4$

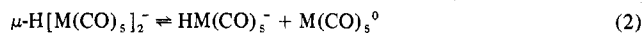
^a Reactant ratios similar to that of the Chatt et al.¹ preparation. ^b NaBH_4 in fivefold excess. ^c Under similar conditions the first-order rate constant for the disappearance of $\text{Ph}_3\text{PCr}(\text{CO})_5$, also to give *trans*-(Ph_3P)₂ $\text{Cr}(\text{CO})_4$, is $(5.73 \pm 0.15) \times 10^{-6} \text{ s}^{-1}$. ^d NaBH_4 in fourfold excess. ^e A somewhat slower rate ($k = 3.02 \times 10^{-4} \text{ s}^{-1}$) and some (Ph_3P) $\text{Mo}(\text{CO})_5$ product observed when this reaction is carried out in air.

observation that carbon-13 labeled CO incorporation was not stereospecific led the authors to suggest that H does not act as a *cis*-labilizing ligand¹⁸ in this compound and that the results support a hydride migration pathway, eq 1.¹⁷



The nature of the "hydride" ligand is expected to be considerably modified in what is essentially an electron-deficient environment. The anion $\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$ is formally isoelectronic with $\text{Mn}_2(\text{CO})_{10}$ ¹⁹ and several mechanistic studies for substitution and decomposition of the latter may be aptly compared with the present data. Substitution reactions of $\text{Mn}_2(\text{CO})_{10}$ to yield $\text{LMn}_2(\text{CO})_9$ and $\text{L}_2\text{Mn}(\text{CO})_8$ were suggested by Basolo and Wawersik to proceed by a simple CO dissociative mechanism.²¹ Poë and co-workers proposed that, in addition to the CO dissociative path, reversible homolytic cleavage, thus producing a solvent-caged radical pair of substitutionally labile $\cdot\text{Mn}(\text{CO})_5$, is also important in the primary kinetic process.²²

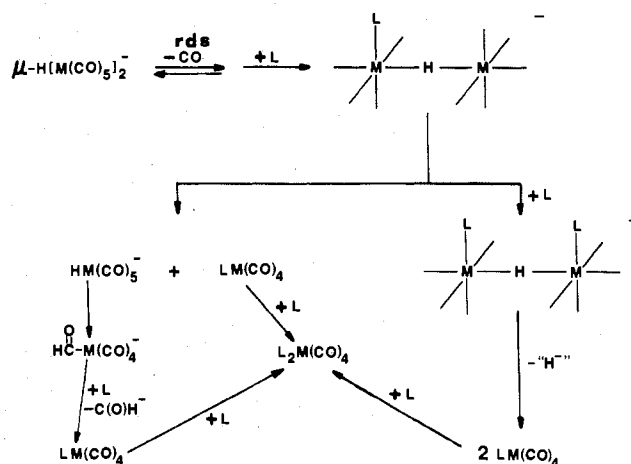
We have made the following observations which would support simple dissociative loss of CO on the intact $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$. The dependence of rates of disappearance of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ in the ligand substitution reactions is first order in carbonylate, and the dependence on the nature of M is in agreement with M-CO bond strengths ($\text{Mo} > \text{Cr} > \text{W}$). The rate of disappearance of the carbonylate in the presence or in the absence of trapping ligands is inhibited by added CO. The rate of reaction is independent of the nature of L and of the concentration of L above a $[\text{L}]/[\text{carbonylate}]$ ratio of 10. The observed neutral reaction products are $\text{L}_2\text{M}(\text{CO})_4$; the production of $\text{M}(\text{CO})_5^0$ according to the heterolytic dimer disruption (eq 2) should lead to $\text{LM}(\text{CO})_5$, which is not



observed in these reactions. However, eq 2 most likely accounts for the metal scrambling reactions yielding $[(\text{OC})_5\text{M}-\text{H}-\text{M}'(\text{CO})_5]^-$ in THF solutions of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$ and $\text{Et}_4\text{N}^+\mu\text{-H}[\text{W}(\text{CO})_5]_2^-$ at 80 °C (presumably in closed systems).⁸ Those reactions, however, are quite slow compared to the ones observed here, attaining equilibrium over a period of 60 h.⁸

Scheme I shows the initial steps that have been substantiated in this present work as well as some speculation on subsequent steps. The scheme shows that the disubstituted neutral products observed in this study may be rationalized either according to further substitution of the intact dimer (right-hand path) or by dimer disruption at the monosubstituted stage

Scheme I



(left-hand path). The point at which disruption of the dinuclear species competes with further substitution of the intact dimer is expected to depend on the electronic and steric environment about the M-H-M bridge. It is conceivable that the flexibility of the M-H-M linkage might allow for increased M-M bond formation as steric effects of the substituent ligands promote bending at that site. This statement is prompted by the observed increased kinetic stability of $\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$ over that of $\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$. Disruption of the dimer must eventually occur, however, and ligand steric effects are expected to play a major role as the degree of substitution increases. (It should be noted that the nature of the bridging ligand is a major influence in this regard. The iodine-bridged $\mu\text{-I}[\text{Cr}(\text{CO})_5]_2^-$ dissociates at room temperature in the presence of PPh_3 to yield $\text{Ph}_3\text{PCr}(\text{CO})_5$ and $\text{ICr}(\text{CO})_5$.²³)

Although the eventual disposition of the H^- is unknown, we feel it reasonable to propose that a formyl species may be involved; for example, see the left-hand path. Since the reversible addition of anions to carbonyls has been verified by studies of $^{18}\text{OH}^-$ addition reactions,²⁴ the simple loss of hydride given by " H^- " in the right-hand path is not inconceivable.

Further work in this area involves synthesis of binuclear complexes of the correct steric/electronic balance to stabilize various intermediates along the path(s).

The final comments are directed toward our initial goal of determining the importance of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ as intermediates in the Chatt synthesis of substituted metal carbonyls. The standard method of preparation of $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ salts is via reaction of NaBH_4 and $\text{M}(\text{CO})_6$ in refluxing THF.⁸ Ethanolic solutions of NaBH_4 and $\text{M}(\text{CO})_6$ also give rise to $\text{Na}^+\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$. For example, after a 15-min reflux of NaBH_4 and $\text{Cr}(\text{CO})_6$ in EtOH, $\nu(\text{CO})$ bands at 2032 (w), 1942 (s), and 1880 (m) cm^{-1} build up in substantial amounts.²⁵ As shown in Table IV, the disappearance of $\text{M}(\text{CO})_6$ in the presence of NaBH_4 and PPh_3 in EtOH is slower than the disappearance of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ in the presence of PPh_3 , also in EtOH solvent. Indeed $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$ decomposes in the absence of ligand in EtOH with a rate still more rapid ($k = 1.70 \times 10^{-4} \text{ s}^{-1}$)⁷ than that of the $\text{Cr}(\text{CO})_6/\text{NaBH}_4/\text{PPh}_3$ reaction. Hence we would not expect to spectroscopically observe the presence of $\text{Na}^+\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ in the Chatt synthesis; it would react as soon as it could be formed. The results show that the intermediacy of a bridging hydride, $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$, in the Chatt synthesis of multiple substituted $\text{L}_x\text{M}(\text{CO})_{6-x}$ compounds, is consistent with its formation, rates of reaction, and products.

Several experiments were directed toward exploring the possibilities of other intermediates in the Chatt synthesis. Although reaction of NaBH_4 and $\text{Cr}(\text{CO})_6$ ultimately leads

to formation of $\text{Na}^+\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$, the first-formed product of this reaction is most likely a formyl complex, which subsequently converts into the bridging hydride. When NaBH_4 is reacted with $\text{Cr}(\text{CO})_6$ in THF at room temperature, over a period of hours, $\nu(\text{CO})$ bands build up at 2021 cm^{-1} (br, w), 1906 (s), 1889 (s), and 1838 (m). These band positions and intensities are very similar to those previously reported for $\text{Cr}(\text{CO})_5\text{C}(\text{O})\text{H}^-$ prepared from $\text{NaHB}(\text{OMe})_3$ or $\text{KHB}(\text{O}-i\text{-Pr})_3$ and $\text{Cr}(\text{CO})_6$ and identified by IR as well as ^1H NMR.²⁶ Our observation is that two products are present prior to the $\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$ formation. The band at 1889 cm^{-1} continues to grow as the remaining absorptions (due to formyl complex presumably) decrease and those due to bridging hydride begin to appear. Whether the formyl complex anion or the second species, which is now in the process of being positively identified,²⁷ might also lead to the substitution products observed when 5A donor ligands are added to the $\text{NaBH}_4/\text{M}(\text{CO})_6$ reaction mixture awaits further investigation on isolated compounds.²⁸

Acknowledgment. The authors appreciate the helpful discussions with Professor D. J. Darensbourg and acknowledge the support of Tulane University.

Registry No. $\mu\text{-H}[\text{W}(\text{CO})_5]_2^-$, 19773-10-5; $\mu\text{-H}[\text{Mo}(\text{CO})_5]_2^-$, 45270-68-6; $\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$, 19571-06-3; $\mu\text{-D}[\text{Cr}(\text{CO})_5]_2^-$, 64599-99-1; $(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4\text{PPh}_3^-$, 64599-98-0; PPh_3 , 603-35-0; *trans*- $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$, 38800-75-8; *cis*- $\text{Mo}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$, 59599-01-8; *cis*- $\text{Cr}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$, 64625-99-6; $\text{P}(\text{OPh})_3$, 101-02-0; PMe_2Ph , 672-66-2; $\mu\text{-D}[\text{Mo}(\text{CO})_5]_2^-$, 64600-04-0; $\text{Et}_4\text{N}^+[(\text{CO})_5\text{MoHM}(\text{CO})_4\text{PPh}_3]^-$, 64600-03-9; $\text{Et}_4\text{N}^+\mu\text{-D}[\text{Cr}(\text{CO})_5]_2^-$, 64600-02-8; $\text{Et}_4\text{N}^+\mu\text{-D}[\text{Mo}(\text{CO})_5]_2^-$, 64600-05-1; THF, 109-99-9; EtOH, 64-17-5; NaBH_4 , 16940-66-2; $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Mo}(\text{CO})_6$, 13939-06-5.

Supplementary Material Available: The infrared spectrum of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$ and assignments as well as representative first-order plots for the thermal decomposition of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$ and $\text{Et}_4\text{N}^+\mu\text{-D}[\text{Cr}(\text{CO})_5]_2^-$ (2 pages). Ordering information is given on any current masthead page.

References and Notes

- J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organomet. Chem.*, **29**, 105 (1971).
- K. -Y. Hui and B. L. Shaw, *J. Organomet. Chem.*, **124**, 262 (1977).
- W. O. Siegl, *J. Organomet. Chem.*, **92**, 321 (1975).
- Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, 829 (1975).
- J. R. Shapley, M. Tachikawa, G. F. Stuntz, and T. B. Keister, 173rd National Meeting, American Chemical Society, New Orleans, La., March 1977.
- M. Y. Darensbourg and J. Inman, unpublished results.
- M. Y. Darensbourg and N. Walker, *J. Organomet. Chem.*, **117**, C68 (1976).
- R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).
- T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).
- R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962).
- W. Hieber and J. Peterhans, *Z. Naturforsch. B*, **14**, 462 (1959).
- J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc. A*, 2796 (1969).
- Although Chatt et al. report the trans geometry for this complex as obtained by their procedure,¹ we have observed that the cis to trans isomerization is effected after long reflux periods. The initial neutral product, $(\text{Ph}_3\text{P})_2\text{Mo}(\text{CO})_4$, is of cis geometry in the Chatt synthesis,¹ in the bridging hydride synthesis reported here, as well as in the Shaw and Hui synthesis.²
- A nearly completed x-ray crystal structure of $\text{Et}_4\text{N}^+\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$, carried out in collaboration with Professor J. L. Atwood, University of Alabama, confirms these stereochemical conclusions.
- R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey, and R. Bau, *J. Am. Chem. Soc.*, **98**, 4491 (1976).
- J. P. Oisen, T. F. Koetzle, S. W. Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974).
- T. L. Brown and B. H. Byers, *J. Organomet. Chem.*, **127**, 181 (1977).
- J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3160 (1976).
- Several neutron-diffraction studies on these systems have shown non-linearity in the M-H-M bond and substantial M-M bond character has been suggested to exist in the bridge.²⁰
- See ref 15 and references therein. See also J. Roziere, J. M. Williams, R. P. Stewart, J. L. Petersen, and L. F. Dahl, *J. Am. Chem. Soc.*, **99**, 4497 (1977).
- H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, **3**, 113 (1969).
- L. I. B. Haines, D. Hopgood, and A. J. Poë, *J. Chem. Soc. A*, 421 (1968); J. P. Fawcett, A. J. Poë, and K. R. Sharma, *J. Am. Chem. Soc.*, **98**, 1401 (1976); J. P. Fawcett, R. A. Jackson, and A. J. Poë, *J. Chem. Soc., Chem. Commun.*, 733 (1975).
- J. K. Ruff, *Inorg. Chem.*, **7**, 1821 (1968).
- D. J. Darensbourg and J. A. Froelich, *J. Am. Chem. Soc.*, **99**, 4727 (1977).
- This statement contrasts with the earlier report that $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ is not readily formed in EtOH.⁷ Tetrahydrofuran is the solvent of choice for synthesis of the anion since its subsequent decomposition is slower in THF.
- C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **98**, 5395 (1976).
- Two of the possibilities for the species which gives rise to the 1889-cm^{-1} band are the well-known $\text{Cr}_2(\text{CO})_{10}^{2-}$ and the less well characterized $\text{HCr}(\text{CO})_5^-$.
- We presently have evidence that the two $\text{M}(\text{CO})_5$ moieties in $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ cannot be treated as isolated entities; i.e., in order to account for the $\nu(\text{CO})$ spectral changes which result upon stereospecific substitution of an equatorial site with ^{13}C O on one $\text{M}(\text{CO})_5$ unit only it is necessary to add small interaction constants across the M-H-M bridge. Thus, the infrared analysis of the triphenylphosphine substituted derivative represents a first-order treatment.