**Figure 12.** Differential scanning calorimetry curve obtained for freshly sublimed Fe[HB(pz)₃]₂.

occuring at 424 K. Measurement of several preparations of Fe[HB(pz)₃]₂ shows that no thermal changes occur below the endothermic peak at 432 K. However, depending on the preparation, this temperature may be as much as 7 K lower but has never been observed at higher temperatures. A simultaneous DTA-TGA analysis of freshly sublimed Fe[HB(pz)₃]₂ revealed no change in mass associated with this endotherm, which is thus assigned to the crystallographic phase transformation.

Jesson et al.[23] noted that the difference in volume for two different spin states can cause a change in crystal structure. The volume of Fe[HB(pz)₃]₂ increases by 10% at the phase transition as indicated by volume expansion measurements. This parallels the 10.5% increase found in the Fe–N bond distance in Fe[HB-(pz)₃]₂ as compared with the Fe[HB(3,5-(CH₃)₂pz)₃]₂ bond distance. As mentioned previously the shattering of the crystals of Fe[H(pz)₃]₂ can be easily observed upon heating them on a melting-point stage. The grinding of a freshly sublimed sample of Fe[HB(pz)₃]₂ reduced the temperature of the endotherm, and hence of the structural phase transition, from 432 K to as low as 409 K and also reduced the size of the endotherm. A similar effect may be observed if Fe[HB(pz)₃]₂ is diluted with zinc.[42] Ap-

parently grinding reduces the "cooperative barrier" to the spin-state transition and the associated phase transition.

A comparison of the temperature of the structural phase transition as revealed by the DSC curve with the other indications of the spin state and structural transition seems to indicate rather different temperature ranges for the phase transition. However, it must be recalled that these results are obtained under quite different conditions. For instance, the Mössbauer spectra are obtained under a vacuum of ca. 1 × 10⁻⁴ Torr whereas the DSC results were obtained under helium at atmospheric pressure. Probably more important, the DSC was obtained at a constant heating rate of 10 K/min or over a period of ca. 15 min. In contrast, the Mössbauer spectra between 300 and 430 K were obtained over a period of several days during which the sample temperature was held constant for up to several hours during the measurement of an individual spectrum.

**Supplementary Material Available:** Table I (magnetic susceptibility results for Fe[HB(pz)₃]₂), Table III (Mössbauer effect hyperfine parameters), Figure 4A (Mössbauer spectra of Fe[HB(pz)₃]₂ obtained between 300 and 400 K fit with two quadrupole doublets), and Figure 5A (Mössbauer spectra of Fe[HB(pz)₃]₂ obtained between 405 and 430 K fit with two quadrupole doublets) (6 pages). Ordering information is given on any current masthead page.

(42) Hutchinson, B. B. Unpublished results.

# Notes

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## Photochemical Reactions of Cp'₂Mo₂(CO)₆ (Cp' = η⁵-C₅H₄CH₃) with Amines. Descriptive Chemistry of the Disproportionation Reactions

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Irradiation of Cp₂Mo₂(CO)₆ in the presence of various phosphines and phosphite ligands leads to disproportionation of the metal–metal-bonded dimer:[3,4]

$$Cp_2Mo_2(CO)_6 + L \xrightarrow{h\nu} CpMo(CO)_3^- + CpMo(CO)_3L^+ \quad (1)$$

$$L = PR_3, P(OR)_3$$
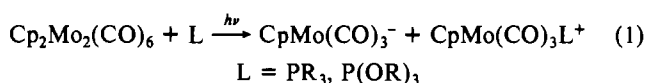
Some time ago, Cox and co-workers[5] reported that irradiation of Cp₂Mo₂(CO)₆ in the presence of pyridine resulted in the formation of the CpMo(CO)₃⁻ complex. It seemed likely that a dispro-

portionation reaction analogous to that with phosphines and phosphites was occurring, but interestingly, no cationic carbonyl-containing product was spectroscopically identified in the reaction solution. We therefore decided to investigate in more detail the photochemical reactions of Cp₂Mo₂(CO)₆ with various amine ligands. Our emphasis was on determining if disproportionation was occurring, and if so, what the cationic product was. Herein we report that some amine ligands do disproportionate the Cp'₂Mo₂(CO)₆ dimer (Cp' = η⁵-C₅H₄CH₃).[6] In those cases where disproportionation occurs, the products observed are dependent on the secondary reactions of the cationic product with the amine.

## Experimental Section

All reactions of air-sensitive materials were performed under a nitrogen atmosphere by employing standard Schlenk techniques. Cp'₂Mo₂(CO)₆,[6,7] [Cp'Mo(CO)₃py][BPh₄],[8] and Mo(CO)₃(py)₃[9] were synthesized according to literature procedures. Except where noted, all solvents were reagent grade. Pyridine (py) and triethylamine (NEt₃) were dried over the appropriate drying agent and distilled under nitrogen.[10] Cyclohexylamine (NH₂(c-Hx); c-Hx = cyclohexyl) and aniline were dried over the appropriate drying agent and vacuum-distilled.[10] Ethylenediamine

(1) University of Oregon.
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(3) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037.
(4) Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4434–4436.
(5) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q.; Pitts, R. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1189–1193.

(6) (η⁵-CH₃C₅H₄)₂Mo₂(CO)₆ was used instead of (η⁵-C₅H₅)₂Mo₂(CO)₆ because the former complex is more soluble in the solvents employed in this study.
(7) Birdwhistle, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.
(8) Burkett-St. Laurent, C. T. R.; Field, J. S.; Haines, R. J.; McMahon, M. *J. Organomet. Chem.* **1979**, *181*, 117–130.
(9) Hieber, W.; Muhlbauer, F. *Z. Anorg. Allg. Chem.* **1935**, *221*, 337–339.
(10) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, U.K., 1966.

**Table I.** Relevant Infrared Data

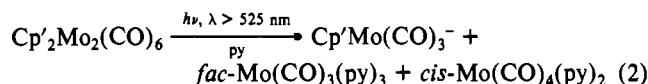| complex | $\nu(C\equiv O)$, cm$^{-1}$ | solvent | ref |
|---|---|---|---|
| Cp'$_2$Mo$_2$(CO)$_6$[a] | 2012, 1952, 1910 | C$_6$H$_6$ | 3 |
| | 2006, 1949, 1904 | py | c |
| | 2009, 1951, 1910 | NH$_2$(c-Hx) | c |
| | 2015, 1957, 1916 | NEt$_3$ | c |
| | 2005, 1946, 1904 | C$_6$H$_5$NH$_2$ | c |
| Cp'Mo(CO)$_3$$^{-}$[a,d] | 1894, 1776 | C$_6$H$_6$ | 3, 12 |
| | 1892, 1775 | py | c |
| | 1892, 1762, 1782 | NH$_2$(c-Hx) | c |
| | 1892, 1776 | en | c |
| [CpMo(CO)$_3$py$^+$]BPh$_4^{-}$[b] | 2061, 2000, 1978 | CH$_2$Cl$_2$ | 8 |
| [Cp'Mo(CO)$_3$py$^+$]BPh$_4^{-}$[a] | 2064, 2000, 1972 | CH$_2$Cl$_2$ | c |
| | 2058, 1989, 1962 | py | c |
| [CpMo(CO)$_2$py$_2^+$]BPh$_4^{-}$[b] | 1997, 1880 | CH$_2$Cl$_2$ | 8 |
| [Cp'Mo(CO)$_2$py$_2^+$]BPh$_4^{-}$[a] | 1986, 1874 | py | c |
| [Cp'Mo(CO)$_2$en$^+$]PF$_6^{-}$ | 1971, 1869 | CH$_3$CN | c |
| Cp'Mo(CO)$_2$(en-$N$)CONHC$_2$H$_4$NH$_2$[a,e] | 1932, 1839 | C$_6$H$_6$ | c, 13 |
| | 1923, 1825 | en | c, 13 |
| Cp'Mo(CO)$_2$(NH$_2$(c-Hx))CONH(c-Hx)[a] | 1931, 1841 | C$_6$H$_6$ | c, 13 |
| | 1930, 1833 | NH$_2$(c-Hx) | c, 13 |
| *fac*-Mo(CO)$_3$(py)$_3$ | 1905, 1775 | py | c, 14 |
| *cis*-Mo(CO)$_4$(py)$_2$ | 2014, 1895, 1882, 1843 | DME | 15 |
| | 2012, 1881, 1878, 1832 | py | c |

[a] Cp' = $\eta^5$-C$_5$H$_4$CH$_3$. [b] Cp = $\eta^5$-C$_5$H$_5$. [c] This work. [d] The cation in C$_6$H$_6$ was Cp'Mo(CO)$_2$(PPh$_3$)$_2^+$. In py, NH$_2$(c-Hx), and en, the cation is discussed in the text. [e] The en-$N$ nomenclature indicates that one nitrogen atom of the en ligand is coordinated to the Mo atom.

(en) (Aldrich Anhydrous Gold Label) was used as received.

All photochemical and dark reactions were monitored by infrared spectroscopy on a Perkin-Elmer 983, Nicolet 5DXB FT-IR, or Beckman 4240 spectrophotometer. $^1$H NMR spectra were obtained with a GE QE-300 NMR spectrometer. The light source used for all irradiations was a 200-W Oriel Co. high-pressure mercury arc lamp. A Corning Glass CS 3-68 filter ($\lambda > 525$ nm) was used for all irradiations. All irradiations were performed in an IR spectroscopy cell with CaF$_2$ windows and monitored in the region 2200–1600 cm$^{-1}$. All reaction solutions were deoxygenated with a nitrogen purge prior to irradiation. Typical reaction solutions consisted of 10$^{-3}$ M Cp'$_2$Mo$_2$(CO)$_6$ in benzene. Reaction products were identified by comparison of their infrared absorption spectra to the spectra of previously reported complexes (Table I).
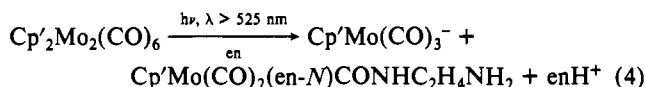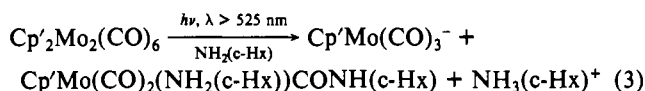
**Results**

Irradiation ($\lambda > 525$ nm) of Cp'$_2$Mo$_2$(CO)$_6$ (10$^{-3}$ M) and pyridine in benzene resulted in the disappearance of Cp'$_2$Mo$_2$(CO)$_6$ and the formation of Cp'Mo(CO)$_3^-$. (A reaction occurred only when the concentration of pyridine in benzene was 50% by volume or higher.[11]) The reaction was monitored by infrared spectroscopy, which showed the disappearance of the Cp'$_2$Mo$_2$(CO)$_6$ bands at 2006, 1949, and 1904 cm$^{-1}$ and the growth of new bands at 1892 and 1775 cm$^{-1}$ (Table I). In addition to the Cp'Mo(CO)$_3^-$ product, *fac*-Mo(CO)$_3$(py)$_3$ was also formed ($\nu(C\equiv O)$ = 1905 and 1775 cm$^{-1}$), along with a small amount of *cis*-Mo(CO)$_4$(py)$_2$ ($\nu(C\equiv O)$ = 2012, 1881, 1878, 1832 cm$^{-1}$). In agreement with the previous report by Allen and co-workers,[5] no bands attributable to the Cp'Mo(CO)$_3$py$^+$ cation (or Cp'Mo(CO)$_2$(py)$_2^+$) were observed. The quantum yield ($\lambda$ = 493 nm) for the reaction of Cp$_2$Mo$_2$(CO)$_6$ with pyridine is 0.79.[5] The (unbalanced) equation representing the observed reaction in pyridine is thus

$$Cp'_2Mo_2(CO)_6 \xrightarrow[\text{py}]{h\nu, \lambda > 525 \text{ nm}} Cp'Mo(CO)_3^- +$$
$$\textit{fac}\text{-Mo(CO)}_3(\text{py})_3 + \textit{cis}\text{-Mo(CO)}_4(\text{py})_2 \quad (2)$$

Irradiation ($\lambda > 525$ nm) of Cp'$_2$Mo$_2$(CO)$_6$ (10$^{-3}$ M) in the presence of either ethylenediamine or cyclohexylamine resulted in the following reactions:

$$Cp'_2Mo_2(CO)_6 \xrightarrow[\text{NH}_2(\text{c-Hx})]{h\nu, \lambda > 525 \text{ nm}} Cp'Mo(CO)_3^- +$$
$$Cp'Mo(CO)_2(NH_2(c\text{-}Hx))CONH(c\text{-}Hx) + NH_3(c\text{-}Hx)^+ \quad (3)$$

$$Cp'_2Mo_2(CO)_6 \xrightarrow[\text{en}]{h\nu, \lambda > 525 \text{ nm}} Cp'Mo(CO)_3^- +$$
$$Cp'Mo(CO)_2(en\text{-}N)CONHC_2H_4NH_2 + enH^+ \quad (4)$$

(Unlike the pyridine reactions, the reactions with en and cyclohexylamine occurred at low ligand concentrations: 10$^{-1}$ M ligand in benzene was typically used. The en-$N$ nomenclature indicates that only one nitrogen atom of the en ligand is coordinated to the Mo atom.) The carbamoyl (carboxamido) reaction products, Cp'Mo(CO)$_2$(NH$_2$(c-Hx))CONH(c-Hx) ($\nu(C\equiv O)$ = 1931 and 1841 cm$^{-1}$) and Cp'Mo(CO)$_2$(en-$N$)CONHC$_2$H$_4$NH$_2$ ($\nu(C\equiv O)$ = 1932 and 1839 cm$^{-1}$), were identified by infrared spectroscopy by comparison with the CpMo(CO)$_2$(NH$_3$)CONH$_2$ complex ($\nu(C-O)$ = 1935 and 1830 cm$^{-1}$).[13]

No reaction occurred when Cp'$_2$Mo$_2$(CO)$_6$ (10$^{-3}$ M) was irradiated ($\lambda > 525$ nm) in benzene solution in the presence of aniline or NEt$_3$.[16]

$$Cp'_2Mo_2(CO)_6 \xrightarrow[\text{NEt}_3 \text{ or aniline}]{h\nu, \lambda > 525 \text{ nm}} \text{no reaction} \quad (5)$$

**Discussion**

**Photochemical Reaction with Pyridine.** The products that form in the photochemical reaction of Cp'$_2$Mo$_2$(CO)$_6$ with pyridine are shown in eq 2. The Cp'Mo(CO)$_3^-$ species is an expected product of the disproportionation reaction, but no infrared bands attributable to the cationic products of the disproportionation reaction (Cp'Mo(CO)$_3$py$^+$ or Cp'Mo(CO)$_2$(py)$_2^+$) were observed. The formation of the *fac*-Mo(CO)$_3$(py)$_3$ and *cis*-Mo(CO)$_4$(py)$_2$ products in the reaction with py was initially surprising because no products analogous to these are formed in the photochemical reactions of Cp$_2$Mo$_2$(CO)$_6$ with phosphines and phosphites. However, work by White and Mawby gives a clue to the origin of these species.[17] These workers reported that CpMo(CO)$_3$-
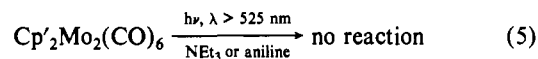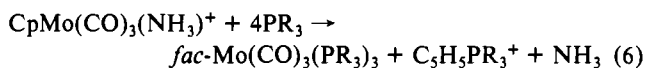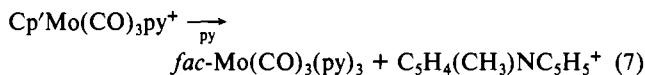
(11) The inability of Cp'$_2$Mo$_2$(CO)$_6$ to react with pyridine at concentrations lower than 50% is probably related to the polarity of the solvent mixture. Previous work of ours showed that, in the reactions of Cp'$_2$Mo$_2$(CO)$_6$ with phosphines, the ionic disproportionation products will back-react in solutions of low polarity.[4] Apparently, at a pyridine concentration of about 50%, the pyridine/benzene solvent mixture is polar enough so that the back-reaction is not a factor. The back-reaction is discussed further in connection with the reactions of Cp'$_2$Mo$_2$(CO)$_6$ with NEt$_3$ and aniline.

(12) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1979**, *90*, 262–268.
(13) Pfister, B. A.; Behrens, H.; Moll, M. *Z. Anorg. Allg. Chem.* **1977**, *428*, 53–60.
(14) Hoff, C. C. *J. Organomet. Chem.* **1985**, *282*, 201–214.
(15) Dessy, E. E.; Wieczorek, L. *J. Am. Chem. Soc.* **1969**, *91*, 4963–4974.

(16) No photochemical reaction with NEt$_3$ or aniline was observed even in neat solutions of the amines. However, it is critical that these amines be carefully purified before use. We found that reactions did occur if the amines were not purified, but the amounts of products and reaction times were variable. No reactions occurred when the amines were carefully purified.

$(NH_3)^+$ ($Cp = \eta^5\text{-}C_5H_5$) reacted with phosphines according to eq 6. This reaction suggests that if $Cp'Mo(CO)_3py^+$ were to form

$$CpMo(CO)_3(NH_3)^+ + 4PR_3 \rightarrow$$
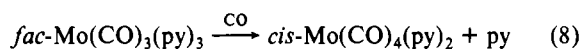$$fac\text{-}Mo(CO)_3(PR_3)_3 + C_5H_5PR_3^+ + NH_3 \quad (6)$$

as the cationic product in the disproportionation reaction, then it might react further with pyridine to form $fac\text{-}Mo(CO)_3(py)_3$. To check this hypothesis, $Cp'Mo(CO)_3py^+$ (13 mg; $2.0 \times 10^{-5}$ mol) was reacted at room temperature with neat pyridine (2 mL) and the reaction monitored by infrared spectroscopy; conversion to $fac\text{-}Mo(CO)_3(py)_3$ (and small amounts of $Cp'Mo(CO)_2(py)_2^+$) occurred within minutes (eq 7) (Table I). Attempts to isolate
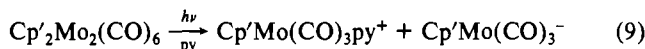
$$Cp'Mo(CO)_3py^+ \xrightarrow{py}$$
$$fac\text{-}Mo(CO)_3(py)_3 + C_5H_4(CH_3)NC_5H_5^+ \quad (7)$$

and identify the $C_5H_4(CH_3)NC_5H_5^+$ product in the disproportionation of $Cp'_2Mo_2(CO)_6$ with pyridine and in reaction 7 were unsuccessful.[18] The exact nature of the displaced cyclopentadienyl ligand in the disproportionation reaction thus remains uncertain.

It remains to explain the source of the small amount of *cis*-$Mo(CO)_4(py)_2$ formed in the photochemical reaction of $Cp'_2Mo_2(CO)_6$ with pyridine. The origin of this product is undoubtedly a reaction of the $fac\text{-}Mo(CO)_3(py)_3$ complex. Experiments showed that *cis*-$Mo(CO)_4(py)_2$ slowly formed (in a dark reaction) when CO was bubbled through a pyridine solution of $fac\text{-}Mo(CO)_3(py)_3$:

$$fac\text{-}Mo(CO)_3(py)_3 \xrightarrow{CO} cis\text{-}Mo(CO)_4(py)_2 + py \quad (8)$$

The free CO probably comes from the decomposition of a small amount of the reactants or products.
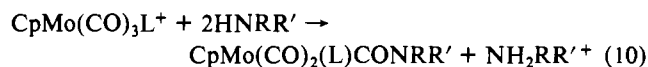
In summary of the reaction with pyridine, the experiments above suggest that the $Cp'_2Mo_2(CO)_6$ complex disproportionates when it is irradiated in the presence of pyridine (eq 9). This reactivity

$$Cp'_2Mo_2(CO)_6 \xrightarrow[py]{h\nu} Cp'Mo(CO)_3py^+ + Cp'Mo(CO)_3^- \quad (9)$$

is analogous to that observed with phosphine and phosphite ligands. However, the cationic product, $Cp'Mo(CO)_3py^+$, is unstable in the presence of pyridine, and the disproportionation reaction is followed by the reactions in eq 7 and 8 to give the observed products.
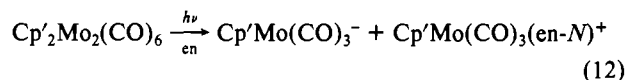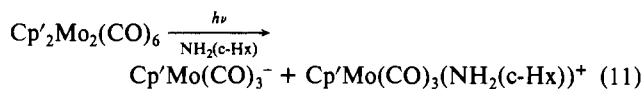
**Photochemical Reactions with Ethylenediamine and Cyclohexylamine.** The products that form in the photochemical reactions of $Cp'_2Mo_2(CO)_6$ with ethylenediamine and cyclohexylamine are shown in eq 3 and 4. As in the reactions with pyridine, the $Cp'Mo(CO)_3^-$ anionic disproportionation product was observed (Table I), but no metal-containing cationic disproportionation products ($Cp'Mo(CO)_3L^+$ or $Cp'Mo(CO)_2L_2^+$) were observed.

The products obtained in these reactions are explained as follows. It is well-known that cationic complexes of the type $CpMo(CO)_3L^+$ (L = $NR_3$, CO; M = Mo, W) react rapidly at room temperature with primary and secondary alkylamines to form carbamoyl complexes:[13,19,20]

$$CpMo(CO)_3L^+ + 2HNRR' \rightarrow$$
$$CpMo(CO)_2(L)CONRR' + NH_2RR'^+ \quad (10)$$

Therefore, we suggest that the $Cp'_2Mo_2(CO)_6$ dimer initially photochemically disproportionates with en and $NH_2(c\text{-}Hx)$ ac-

cording to reactions 11 and 12, respectively. The cationic products

$$Cp'_2Mo_2(CO)_6 \xrightarrow{h\nu}{NH_2(c\text{-}Hx)}$$
$$Cp'Mo(CO)_3^- + Cp'Mo(CO)_3(NH_2(c\text{-}Hx))^+ \quad (11)$$

$$Cp'_2Mo_2(CO)_6 \xrightarrow[en]{h\nu} Cp'Mo(CO)_3^- + Cp'Mo(CO)_3(en\text{-}N)^+$$
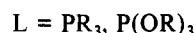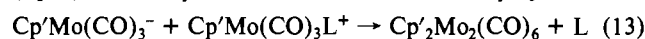$$(12)$$

are not stable, and the disproportionation reaction is followed by reactions similar to eq 10 to give the observed carbamoyl reaction products.

As further confirmation of the hypothesis above, we observed that the $Cp'Mo(CO)_3py^+$ cation reacted with en or $NH_2(c\text{-}Hx)$ to form the carbamoyl products, $Cp'Mo(CO)_2(py)\text{-}CONHC_2H_4NH_2$ ($\nu(C{\equiv}O)$ = 1932 and 1833 $cm^{-1}$) and $Cp'Mo(CO)_2(py)CONH(c\text{-}Hx)$ ($\nu(C{\equiv}O)$ = 1930 and 1836 $cm^{-1}$), respectively.[22]

The amount of $Cp'Mo(CO)_3^-$ formed in the disproportionation reaction with en was measured as a check on the proposed reaction stoichiometry. Irradiation for several minutes of 0.0153 M $Cp'_2Mo_2(CO)_6$ and 0.1 M en in acetonitrile resulted in the disappearance of $4.8 \times 10^{-3}$ M dimer and the formation of $4.4 \times 10^{-3}$ M $Cp'Mo(CO)_3^-$. This ratio of 1.0 $Cp'_2Mo_2(CO)_6$ consumed to 0.92 $Cp'Mo(CO)_3^-$ formed (essentially 1:1) is consistent with the proposed mechanism. The reaction was carried out in an infrared cell, and the following bands and extinction coefficients were used to determine the stoichiometry: $Cp'_2Mo_2(CO)_6$, 1953 $cm^{-1}$, $\epsilon$ = 5400; $Cp'Mo(CO)_3^-$, 1772 $cm^{-1}$, $\epsilon$ = 4200.

**Photochemical Reactions with Aniline and Triethylamine.** No reaction occurred when $Cp'_2Mo_2(CO)_6$ ($10^{-3}$ M) was irradiated ($\lambda$ > 525 nm) in benzene solution in the presence of aniline or $NEt_3$.[16] We recently showed that the apparent unreactivity of the $Cp'_2Mo_2(CO)_6$ complex toward photochemical disproportionation with some phosphine and phosphite ligands can be attributed to a facile back-reaction of the disproportionation products (eq 13).[4] One explanation for the lack of a net disproportionation

$$Cp'Mo(CO)_3^- + Cp'Mo(CO)_3L^+ \rightarrow Cp'_2Mo_2(CO)_6 + L \quad (13)$$

$$L = PR_3, P(OR)_3$$

reaction with aniline and $NEt_3$ may be the occurrence of a similar facile back-reaction of the ionic disproportionation products to re-form the $Cp'_2Mo_2(CO)_6$ dimer.

In some instances the disproportionation back-reactions can be prevented by one of the following methods: (1) a more polar solvent can be used (e.g. $CH_2Cl_2$; a more polar solvent stabilizes the ionic products)[4] or (2) the cationic or anionic products can be reacted further so as to remove them from use in the back-reaction.[4,23] Neither of these methods was successful in demonstrating that a disproportionation reaction was occurring in the reactions with $NEt_3$ or aniline. Thus, repeating the photochemical reactions of $Cp_2Mo_2(CO)_6$ with $NEt_3$ or aniline in $CH_2Cl_2$ did not lead to any net reaction (method 1). And, as explained in the following paragraph, neither the $Cp'Mo(CO)_3(NEt_3)^+$ nor the $Cp'Mo(CO)_3(aniline)^+$ complex is capable of further reaction (method 2).

In this study, a net reaction of $Cp'_2Mo_2(CO)_6$ with amines occurred only when the cationic products were able to undergo further reaction (method 2). In the case of en and cyclohexylamine, the cation formed carbamoyl products, and in the case of pyridine, the cation reacted according to eq 7. No net disproportionation occurred with $NEt_3$ or aniline because similar reactions are not possible with these amines. Thus, $NEt_3$ will not react to form the carbamoyl complex[19] because it is a tertiary amine, and Angelici showed that aniline and other aromatic amines do not react to form carbamoyl complexes.[24] In addition, neither of these amines reacted as pyridine did in eq 7. This result is not

(17) White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261–266.
(18) NMR and IR analyses were unable to detect this species in situ. In addition, electron impact and FAB mass spectroscopies were unable to detect this species. A Chemical Abstracts Online structure search could not find this cation.
(19) Jetz, W.; Angelici, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3799–3802.
(20) Angelici reported that in some cases the metal carbamoyls will react further with primary amines to form $Cp'Mo(CO)_3^-$ and a urea.[19,21] We did not observe this reactivity in our systems.
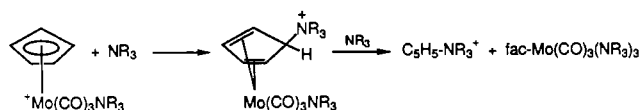(21) Dombek, B. D.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *134*, 203–217.

(22) The products were identified by infrared spectroscopy.[13] We can identify the products as substituted carbamoyls, but the pyridine ligands in the products may be replaced by $NH_2(c\text{-}Hx)$ or en-$N'$.
(23) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253–258.
(24) Angelici, R. *Acc. Chem. Res.* **1972**, *5*, 335–341.

unexpected because neither NEt$_3$ nor aniline is as nucleophilic as pyridine. The nucleophilicity of the amine is the key property in this type of reaction because reaction 7 is proposed to proceed by nucleophilic attack on the Cp ring:[17]



Apparently neither aniline nor NEt$_3$ is nucleophilic enough for this step to occur. Control experiments are consistent with this suggestion; no reaction was observed between Cp$'$Mo(CO)$_3$py$^+$ and aniline in benzene solution.

In summary of the results with NEt$_3$ and aniline, Cp$'_2$Mo$_2$(CO)$_6$ does not give net disproportionation products when irradiated in the presence of these ligands. The unreactivity is probably the result of a facile back-reaction of the disproportionation products to re-form the Cp$'_2$Mo$_2$(CO)$_6$ dimer. That the back-reaction occurs is a consequence of the inability of the cationic product to react with these amines to form other products.

**Conclusions.** Cp$'_2$Mo$_2$(CO)$_6$ will disproportionate in a photochemical reaction with amines only when the cationic product of the reaction, Cp$'$Mo(CO)$_3$(amine)$^+$, can undergo further reaction. By reacting further, the cation is prevented from undergoing a back-reaction with the Cp$'$Mo(CO)$_3^-$ product. A net reaction occurs with pyridine because the Cp$'$Mo(CO)$_3$py$^+$ product reacts with pyridine according to eq 7. A net reaction occurs with ethylenediamine and cyclohexylamine because the cationic disproportionation products react to form carbamoyl complexes (eq 10). No net disproportionation reactions occur with NEt$_3$ or aniline because these amines are not nucleophilic enough to react according to eq 7 and they are incapable of forming carbamoyl complexes.

**Registry No.** Cp$'_2$Mo$_2$(CO)$_6$, 33056-03-0; py, 110-86-1; Cp$'$Mo-(CO)$_3^-$, 64799-62-8; *fac*-Mo(CO)$_3$(py)$_3$, 66701-87-9; *cis*-Mo(CO)$_4$(py)$_2$, 16742-99-7; en, 107-15-3; NH$_2$(c-Hx), 108-91-8; Cp$'$Mo(CO)$_2$(NH$_2$(c-Hx))CONH(c-Hx), 123265-02-1; Cp$'$Mo(CO)$_2$(en-*N*)CONH$_2$C$_2$H$_4$NH$_2$, 123265-03-2; NH$_2$Ph, 62-53-3; NEt$_3$, 121-44-8; Co$'$Mo(CO)$_3$py$^+$, 123265-04-3.

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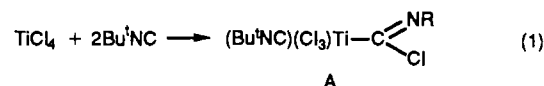Università di Parma, I-43100 Parma, Italy

## Isocyanide Complexes of Titanium(IV) and Vanadium(V): Concerning the Nonexistent Insertion of Isocyanides into a Metal–Chloride Bond

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The addition of isocyanides to high-valent early-transition-metal halides is a known reaction reported in a number of papers[1] and reviewed recently.[2] In the specific case of titanium(IV) chloride, as in a few others, the reaction was often claimed to lead to the formation of a Ti–C functionality derived from the insertion of

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RNC into a Ti–Cl bond.[1] The role of TiCl$_4$ promoting the addition of isocyanides to a carbonylic function in a modified version of the Passerini reaction[3] was interpreted on the basis of the intermediate formation of the iminochloride functionality shown in complex A.[4,5]

$$\text{TiCl}_4 + 2\text{Bu}^t\text{NC} \longrightarrow (\text{Bu}^t\text{NC})(\text{Cl}_3)\text{Ti}-\text{C} \begin{smallmatrix} \nearrow \text{NR} \\ \searrow \text{Cl} \end{smallmatrix} \quad (1)$$

**A**

This assumption was maintained in spite of Lippard's results[6] showing that the reaction of Bu$^t$NC with VCl$_3$ simply leads to the [VCl$_3$(Bu$^t$NC)$_3$] adduct, instead of forming an inserted product. In the search for a structural confirmation of the unusual genesis of the organometallic functionality in reaction 1, we reconsidered the reaction of TiCl$_4$ with isocyanides. Since the isocyanides add to less acidic titanium chlorides derivatives without any insertion occurring,[7] we believed that the metal acidity might be, as suggested,[2] a major factor determining the insertion of RNC into a metal–chloride bond. Therefore, in addition to TiCl$_4$, we considered the vanadium(V) derivative [PhNVCl$_3$(THF)$_2$].

### Results and Discussion

The reaction of TiCl$_4$ with Bu$^t$NC, carried out in toluene, gave, independent of the Ti:RNC ratio, the *cis*-diisocyanide adduct [TiCl$_4$(Bu$_t$NC)$_2$] (1) (85%).[8] When reaction 2 is carried out with



$$\text{TiCl}_4 + 2\text{Bu}^t\text{NC} \longrightarrow \quad (2)$$

**1**
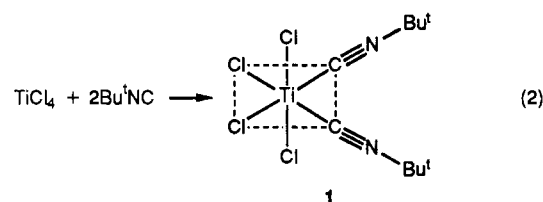
a 1:1 Ti:RNC molar ratio, the excess of TiCl$_4$ remains unreacted in solution. The role of TiCl$_4$ left in solution should be eventually considered in the modified Passerini reaction, in case it is carried out by using a 1:1 Ti:RNC ratio.[4] The nature of R, however, is crucial in determining the RNC:TiCl$_4$ ratio, due either to steric factors or to the presence of donor atoms in its skeleton. We found, in fact, that [TiCl$_4$(2,6-Me$_2$C$_6$H$_3$NC)]$_2$[8] and [TiCl$_4$(C≡NCH$_2$P(O)(OEt)$_2$)]$_2$[8] are dimers containing one isocyanide ligand per titanium. In none of them, however, the insertion of the –N≡C functionality in the Ti—Cl bond was found.[8] The IR spectrum of **1** both in the solid state and in solution showed a single sharp band at 2226 cm$^{-1}$ in Nujol and at 2210 cm$^{-1}$ in CH$_2$Cl$_2$. A sharp singlet for the Bu$^t$ groups is found in the $^1$H NMR at $\delta$ 1.59 (CD$_2$Cl$_2$). There are no additional bands appearing in the 1600–1700-cm$^{-1}$ region, unless the IR spectrum is taken in the air or the solid exposed briefly to the air. Figure 1 shows the Nujol

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(1) Crociani, B.; Nicolini, M.; Richards, R. L. *J. Organomet. Chem.* **1975**, *101*, C1. Benham-Dahkordy, M.; Crociani, B.; Nicolini, M.; Richards, R. L. *Ibid.* **1979**, *181*, 69. Crociani, B.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1973**, 127. Benham-Dahkordy, M.; Crociani, B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2015.

(2) Crociani, B. Reactions of Coordinated Isocyanides. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; p 553.

(3) Passerini, M. *Gazz. Chim. Ital.* **1921**, *51*, 126, 181.

(4) Seebach, D.; Adam, G.; Gees, T.; Shiess, M.; Weigand, W. *Chem. Ber.* **1988**, *121*, 507 and references therein.

(5) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 871.

(6) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

(7) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1954. Razavi, A.; Mallin, D. T.; Day, R. O.; Rausch, M. D. *J. Organomet. Chem.* **1987**, *C48*, 333.

(8) The synthesis of [TiCl$_4$(2,6-Me$_2$C$_6$H$_3$NC)]$_2$ [$\nu$(C≡N) (Nujol), 2210 cm$^{-1}$] and [TiCl$_4$(C≡NCH$_2$P(O)(OEt)$_2$)]$_2$ [$\nu$(C≡N) (Nujol), 2245 cm$^{-1}$] have been carried out from a CH$_2$Cl$_2$ solution of TiCl$_4$. The isolated compounds have analytical and spectroscopic data in agreement with the proposed formula. The X-ray analysis is currently being carried out on both compounds.