piciously similar ($PdCl_4{}^{2-}$, 0.90 M^{-1} sec^{-1}; Hg(II) 1.2 M^{-1} sec^{-1}). It appears from the reported data[9] that this rate constant in the Hg(II) system should be more on the order of $\simeq 10^3$ which would then appear to be in accord with the observed kinetics. The rate constants for the methyl transfer step differ by $\sim 10^4$ ($PdCl_4{}^{2-}$, 7.7 $\times$ 10^{-3} M^{-1} sec^{-1}; Hg(OAc)$_2$, 85 and 310 M^{-1} sec^{-1}).[1,9] To be sure, in comparing these systems, one must recognize that conditions are quite different. However, the Hg(II) species is clearly more electrophilic than $PdCl_4{}^{2-}$ and also produces slightly more of the "base-off" species, both factors contributing to the more facile methyl transfer process in the case of Hg(II).

Reactions of Transition Metal Dihydrides. V.[1] Interaction of (η-C$_5$H$_5$)$_2$MH$_2$ (M = Mo and W) with Azo or Diazo Compounds

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Abstract: Reaction of Cp$_2$MoH$_2$ (Cp = η-C$_5$H$_5$) with an excess of azobenzene, methyl or ethyl azodicarboxylate, and azodibenzoyl proceeds *via* an incipient formation of hydridohydrazino complexes, Cp$_2$MoH[σ-N(R)NHR], to a π-complex, Cp$_2$Mo(PhN=NPh), or metalloheterocycles, Cp$_2$MoN(COR)N=C(R)O (R = Ph, OMe, OEt). 4-Phenyl-1,2,4-triazoline-3,5-dione behaves differently to give a novel metalated heterocycle, Cp$_2$Mo[σ-NN=C(OH)N(Ph)CO]$_2$. A diazoalkane complex, Cp$_2$Mo(diazofluorene), was also prepared from Cp$_2$MoH$_2$.

W e have reported[2] a detailed study of the interaction of Cp$_2$MoH$_2$ (**1**) or Cp$_2$WH$_2$ (**2**) (Cp = η-C$_5$H$_5$) with carbon–carbon homounsaturation. Novel hydrido–σ-alkyl complexes, Cp$_2$Mo(H)CCH, olefin, or acetylene complexes, Cp$_2$Mo(Un), were isolated and characterized. Stereochemistry and mechanism of the stoichiometric olefin hydrogenation were also investigated which lend an important insight into catalytic hydrogenation. In view of the well-known activity[3] of some molybdenum complexes toward chemical as well as biological nitrogen fixation, it seems important to investigate the interactions between heterounsaturation, e.g., –N=N– or dinitrogen and the dihydrides. Our preliminary study[4] with azobenzene or azodicarboxylates has now been extended to other azo or diazo compounds and the results are summarized here. In the course of our study, a closely related reaction of [Cp$_2$Mo] or [(Me$_5$C$_5$)$_2$Mo] with dinitrogen was reported by Thomas and Brintzinger.[5]

Interactions of various azo or diazo compounds with many d^8 or d^{10} complexes of group VIII elements have been actively investigated in our[6,7] and in several other laboratories.[8-19] The present study will serve to correlate or compare the unique behavior of group VI metal complexes with that of group VIII metal compounds.

Results

The reaction of *trans*-azobenzene with **1** was slow at room temperature, being incomplete even after 2 days.

(1) For Part IV see A. Nakamura and S. Otsuka, *Tetrahedron Lett.* 4529 (1973).

(2) (a) A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **94**, 1886 (1972); (b) A. Nakamura, Abstracts, 5th International Conference on Organometallic Chemistry, Moscow, 1971, Vol. 2, p 550; (c) A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **95**, 7262 (1973).

(3) (a) G. N. Schrauzer, G. Schlesinger, and P. A. Doemeny, *J. Amer. Chem. Soc.*, **93**, 1803 (1971); (b) G. N. Schrauzer, G. W. Kiefer, P. A. Doemeny, and H. Kisch, *ibid.*, **95**, 5582 (1973); (c) E. E. van Tamelen, J. A. Gladyzs, and J. S. Miller, *ibid.*, **95**, 1347 (1973); (d) for recent reviews, M. E. Vol'pin and V. B. Shur, "Organometallic Reaction," Vol. 1, E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N. Y., 1970, p 55; R. W. F. Hardy, R. C. Burns, and G. W. Parshall, "Inorganic Biochemistry," Vol. 2, G. L. Eichhorn, Ed., Elsevier, Amsterdam, 1973, p 787.

(4) S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Commun.*, 1148 (1969).

(5) J. L. Thomas and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1386 (1972); J. L. Thomas, *ibid.*, **95**, 1838 (1973).

(6) S. Otsuka, A. Nakamura, T. Koyama, and Y. Tatsuno, *J. Chem. Soc., Chem. Commun.*, 1105 (1972); *Justus Liebigs Ann. Chem.*, in press.

(7) (a) S. Otsuka, T. Yoshida, and Y. Tatsuno, *Chem. Commun.*, 68 (1971); *J. Amer. Chem. Soc.*, **93**, 6462 (1971); (b) R. S. Dickson, J. A. Ibers, S. Otsuka, and Y. Tatsuno, *ibid.*, **93**, 4636 (1971).

(8) H. F. Klein and J. F. Nixon, *Chem. Commun.*, 42 (1971).

(9) F. M. Hussein and A. S. Kassenally, *J. Chem. Soc., Chem. Commun.*, 3 (1972).

(10) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, **12**, 2290 (1973), and references cited therein.

(11) (a) J. Chatt, G. A. Heath, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 444 (1972); (b) J. Chatt and J. R. Dilworth, *ibid.*, 549 (1972).

(12) A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2248 (1969).

(13) R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 2138, 2141 (1972), and references cited therein.

(14) F. W. B. Einstein, A. B. Gilchrist, G. W. RaynorCanham, and D. Sutton, *J. Amer. Chem. Soc.*, **94**, 645 (1972).

(15) J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1805 (1972).

(16) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometal. Chem.*, **31**, 275 (1971); **40**, 393 (1972).

(17) M. I. Bruce, B. L. Goodal, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 558 (1973).

(18) K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 176 (1973).

(19) (a) P. C. Ellgen and S. L. McMullin, *Inorg. Chem.*, **12**, 2004 (1973); (b) H. Alper, *ibid.*, **11**, 976 (1972).

Table I. Analytical and Some Physical Data

| Compd	Color	Mp, °C	C,[a] %	H, %	N, %	Selected ir data (in cm⁻¹) with assignment
Cp₂Mo(PhN=NPh)	Dark red	155–157	64.93 (64.71)	5.03 (4.94)	7.03 (6.86)	1580, 1260, 1236, 1160, 1070, 1015, 830, 805, 750, 693
Cp₂MoH[N(CO₂C₂H₅)NHCO₂C₂H₅]	Yellow	135 dec	47.47 (47.78)	5.47 (5.51)	6.83 (6.96)	3200 (NH), 1860 (MoH), 1700 (C=O)
Cp₂Mo[(CO₂CH₃)NNCO₂CH₃]	Reddish brown	200 dec	44.84 (45.17)	4.22 (4.34)	7.46 (7.53)	1652 (C=O), 1604 (C=N)
Cp₂Mo[(CO₂C₂H₅)NNCO₂C₂H₅]	Reddish brown	200–230 dec	47.96 (48.01)	4.90 (5.04)	7.02 (7.00)	1650 (C=O), 1600 (C=N)
Cp₂Mo[(COPh)NNCOPh]	Brownish orange	230–240 dec	62.19 (62.08)	4.31 (4.34)	5.92 (6.03)	1590 (C=O), 1557 (C=N)
Cp₂W[(COPh)NNCOPh]	Brownish orange	145–155 dec	52.38 (52.20)	3.62 (3.65)	5.00 (5.07)	1595 (C=O), 1570 (C=N)
Cp₂Mo[NN=C(OH)N(Ph)CO]₂	Reddish brown	293–295	53.52 (53.99)	3.79 (3.83)	14.25 (14.53)	3490, 3440 (OH), 1720, 1630 (C=N or C=O)

[a] Calculated values in parentheses.

Table II. ¹H Nmr Spectra

Compd (solv)	Chemical shifts in δ (ppm, TMS)	Area	Multiplicity[a] (J in Hz)	Assignment
Cp₂Mo(PhN=NPh)	4.8	10	s	Cp
(CS₂)	6.2–7.0	10	m	Ph
Cp₂MoH[N(CO₂CH₃)NHCO₂CH₃]	−8.00	1	s	Mo–H
(CDCl₃)	3.51	3	s	CH₃
	3.63	3	s	CH₃
	5.02	10	s	Cp₃
	5.89	1	br	NH
Cp₂MoH[N(CO₂C₂H₅)NHCO₂C₂H₅]	−8.60	1	s	Mo–H
(CDCl₃)	1.22	3	t(J = 7.5)	CH₃
	1.26	3	t(J = 7.5)	CH₃
	3.9	1	br	NH
	4.00	2	q(J = 7.5)	CH₂
	4.28	2	q(J = 7.5)	CH₂
	5.02	10	s	Cp
Cp₂Mo[(CO₂CH₃)NNCO₂CH₃]	3.57	3	s	CH₃
(CD₃OD)	3.65	3	s	CH₃
	5.49	10	s	Cp
Cp₂Mo[(CO₂C₂H₅)NNCO₂C₂H₅]	1.20	3	t(J = 7.5)	CH₃
(CDCl₃)	1.28	3	t(J = 7.5)	CH₃
	4.04	2	q(J = 7.5)	CH₂
	4.12	2	q(J = 7.5)	CH₂
	5.49	10	s	Cp
Cp₂Mo[(COPh)NNCOPh]	5.00	10	s	Cp
(CDCl₃)	7.30	7	m	Ph
	7.75	5	s	Ph
Cp₂Mo[NN=C(OH)N(Ph)CO]₂	5.86	10	s	Cp
((CD₃)₂SO)	7.2–7.5	10	m	Ph
	9.47[b]	2	s	OH

[a] Key: s, singlet; t, triplet; q, quartet; m, multiplet; br, broad. [b] This peak disappears on addition of D₂O.

When the reaction mixture was heated up to 70° in THF, an azobenzene complex, Cp₂Mo(PhN=NPh), and hydrazobenzene formed. A hydrido–hydrazino complex, Cp₂MoH[N(Ph)NHPh], is a probable intermediate but its isolation has not yet been possible due to the concurrent formation of the final products. Such an intermediate was isolated in the reaction with azodicarboxylates (*vide infra*). The reaction with Cp₂-WH₂ (2) under the same conditions resulted in recovery of starting materials. The azobenzene complex (3) is

Cp₂MoH₂ + PhN=NPh ⟶ Cp₂Mo

with structure:

Ph
|
NNHPh
/
Cp₂Mo
\
H

PhN=NPh ⟶
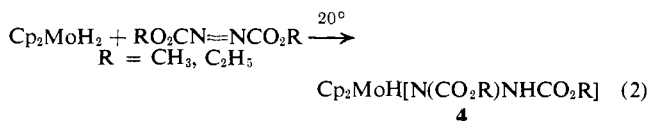
Cp₂Mo(PhN=NPh) + PhNHNHPh   (1)

3
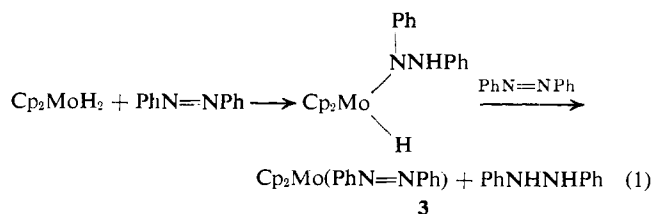
air stable even in solution and yields azobenzene when oxidatively decomposed with an excess of iodine in CCl₄ (Table I). An attempted substitution of the ligand with a strongly chelating diphosphine, (Ph₂-PCH₂)₂, at 120°, however, failed. The nmr spectrum of **3** showed the presence of ten equivalent π-Cp protons and ten monosubstituted phenyl protons. The chemical shift of the Cp protons suggests electron drainage into the azobenzene ligand (*cf.* Table II). An upfield shift of the phenyl protons relative to that of free azobenzene also supports the conclusion. An observation of the strong molecular ion in the mass spectrum also shows strong bondings between the metal and azobenzene.

cis-Azobenzene or its para-substituted derivatives are catalytically isomerized to the trans isomer at 10–30° in the presence of **1** or **2**. The catalysis indicates an interaction prior to the insertion reaction. A de-

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tailed study of the isomerization with various d^8 or d^{10} complexes as catalysts will be described separately.
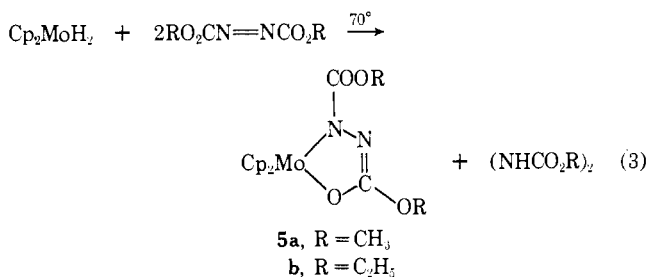
Azomethane is quite unreactive toward **1** or **2** below 100° in solution. The reaction at 150° (in an ampoule) gave a brown unidentifiable insoluble solid whose structure is apparently different from that of **3**.

An equimolar reaction between **1** and dimethyl or diethyl azodicarboxylate in ethanol at room temperature proceeds readily to give an air-sensitive insertion product, **4**. The structure was inferred from the

$$Cp_2MoH_2 + RO_2CN\!\!=\!\!NCO_2R \xrightarrow{20°}$$
$$R = CH_3, C_2H_5$$

$$Cp_2MoH[N(CO_2R)NHCO_2R] \quad (2)$$
$$\mathbf{4}$$

analytical, ir, and ^{1}H nmr data (*cf.* Tables I and II). A similar monoinsertion product, $Cp_2MoH[CH(CO_2\text{-}CH_3)CH_2CO_2CH_3]$, was prepared from **1** and dimethyl fumarate or maleate.[2] In contrast to the hydrido–σ-alkyl complex, the corresponding hydrido–hydrazino complexes (**4**) are remarkably thermally stable (decomposition at 135° in nitrogen) implying its moderate ionic character of the Mo–H bond.

Thermal decomposition of **4** in refluxing THF and with excess azodicarboxylate gave a dark brown turbid solution after 1 hr. Chilling the mixture and subsequent slow crystallization from methanol yielded a reddish brown analytically pure sample, **5a**. N,N'-Dicarbomethoxyhydrazine was also isolated. The ^{1}H nmr spectrum (*cf.* Table II) showed two different methoxy groups. Consistently, two very strong ir bands were observed at 1652 and 1604 cm^{-1} ($\nu_{C=O}$ or $\nu_{C=N}$). These data coupled with the X-ray structure[10] of (Ph$_3$-P)$_2$Pt(PhCONNCOPh), which has a planar metalloheterocycle, PtNN=CO, suggest the presence of a similar metalloheterocycle for this compound. Delocalization of the metal electron into the heterocyclic ligands is shown by the deshielding of the η-C$_5$H$_5$ proton signal (at δ 5.5 ppm) as compared with that of the dihydride (η-C$_5$H$_5$ at δ 4.4 ppm). The structure below is thus proposed.

$$Cp_2MoH_2 + 2RO_2CN\!\!=\!\!NCO_2R \xrightarrow{70°}$$

$$+ (NHCO_2R)_2 \quad (3)$$

5a, R = CH$_3$
**b**, R = C$_2$H$_5$

The formulation (**5a**, **5b**) may suggest that the nitrogen lone pair at the coordinating N atom is stereochemically active enough to cause the two Cp rings to be nonequivalent. However, extensive π delocalization within the metallocycle would make the N atom nearly planar, *e.g.*, N atom in N(SiMe$_3$)$_3$. A related platinum metalloheterocycle, (PPh$_3$)$_2$Pt[(COPh)NNCO-Ph], has an almost planar coordinating N atom as revealed by the X-ray analysis.[10] The novel complex is soluble in polar hydroxylic solvents, *e.g.*, water or methanol, to give an orange air-stable solution. An analogous ethyl ester, **5b**, was also prepared similarly starting from ethyl azodicarboxylate. The electronic

spectrum shows a strong maximum at 355 nm (ϵ 2260) in water. The mass spectra confirm the monomeric nature of the complex exhibiting strong parent peaks for **5a** or **5b**. Fragment ions such as (C$_5$H$_5$)$_2$-MoN(CH$_3$)N=C(OCH$_3$)O, (C$_5$H$_5$)$_2$MoNCO, (C$_5$H$_5$)$_2$-Mo(CH$_3$) or (C$_5$H$_5$)$_2$Mo(NOH), and (C$_5$H$_5$)$_2$MoCH$_2$ or (C$_5$H$_5$)$_2$MoN are observed. The complexes, **5**, show remarkable thermal and air stability. It is stable in air up to ~200° and resists an attack of concentrated aqueous acid or alkali. No evolution of dinitrogen from the heterocyclic system was observed upon heating the aqueous or methanolic solution.

Azodibenzoyl reacts with **1** or **2** in toluene even below room temperature affording dibenzoylhydrazine as a precipitate. The filtered solution gives a molybdenum complex as brownish orange air-stable crystals (**6**) upon evaporation of the solution (Scheme I).

Scheme I

6a, M = Mo
b, M = W
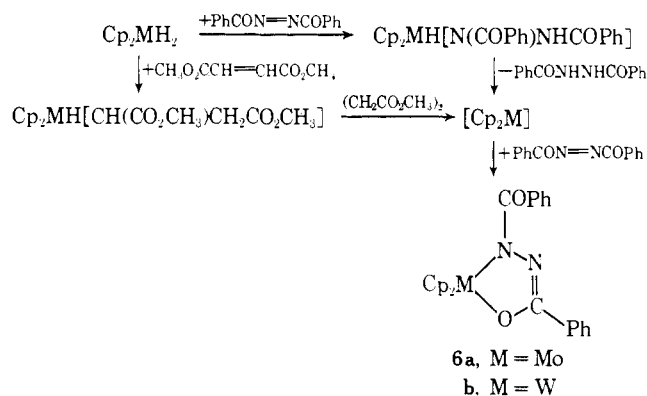
The ir spectra show two strong bands around 1590 and 1560 cm^{-1} suggesting its similar bonding scheme as observed for **5**. The ^{1}H nmr data are not informative but support the composition. The striking similarity of **6a** and **6b** in its color, air stability, and ir spectra indicates that they are isostructural.

It appears that a reactive species, Cp$_2$Mo, derived from the insertion product Cp$_2$MoH[N(COPh)NH-COPh], leads to the formation of **6a**. The species Cp$_2$Mo can be generated, *in situ*, by slow decomposition of a hydrido–σ-alkyl complex, Cp$_2$MoH[CH(CO$_2$-CH$_3$)CH$_2$CO$_2$CH$_3$], and can be trapped as Cp$_2$Mo-(CO)[5] in the decomposition under gaseous CO. The thermal decomposition of Cp$_2$MoH[CH(CO$_2$CH$_3$)CH$_2$-CO$_2$CH$_3$] in the presence of azodibenzoyl gave **6a** in a good yield with a trace amount of N,N'-dibenzoylhydrazine. Reaction of **2** with azodibenzoyl is also expected to proceed *via* intermediacy of Cp$_2$W which might react with aromatic solvents (ArH) to form Cp$_2$WH(Ar). Absence of the hydrido–σ-aryl complex in the product formed in toluene indicates that azodibenzoyl is more reactive to Cp$_2$W than the solvent itself.

Protonation of the heterocyclic complexes, **6a** and **6b**, occurs readily by dissolution in concentrated HCl or DCl giving a brown solution. On standing, a gray precipitate of dibenzoylhydrazine and deep brown crystals of Cp$_2$MoCl$_2$ (when powdered pale green) slowly appeared in the solution. Examination by ^{1}H nmr spectrum of the fresh filtered solution in concentrated DCl showed Cp proton signals at δ (ppm from TMS) 6.35 and 6.65 (intensity ratio, 3:2) for **6a** and δ 6.22 and

6.56 (intensity ratio 3:1) for **6b**. These signals may be attributed to the protonated complexes with different protonation sites. Protonation on the metal is rejected by the absence of ¹H nmr peaks (taken in concentrated HCl) at the usual metal hydride region. Exact site of protonation is not clear but is probably on the N and O atom of the ligand. Reddish brown crystals of composition, Cp₂Mo[(COPh)NNCOPh]·HCl·3H₂O, were obtainable by dissolution of **6a** in concentrated HCl. The ir spectrum (strong bands at 1580 and 1555 cm⁻¹) indicated protonation on the heterocyclic ring. The protonation on the ligand seems to weaken the essentially ionic metal–ligand bonding for
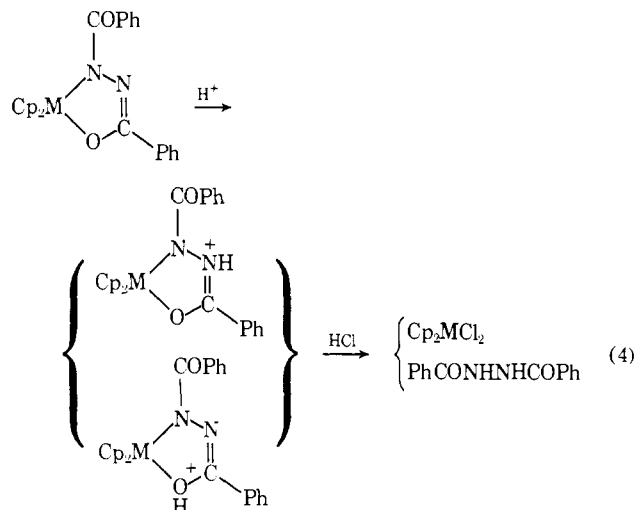

protolytic cleavage. The combined results indicate an ionic nature of the Mo–O or Mo–N bonding in these heterocyclic complexes (**5, 6**) and support its formulation as a Mo(IV) or W(IV) complex (A) rather than a Mo(II) or W(II) complex (B) containing a chelate, –N=NC=O. The conclusion confirms high electron donating ability of the metal in the unstable Cp₂M species.
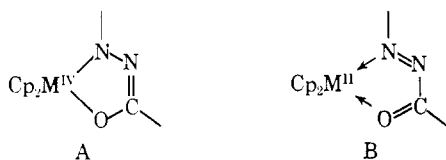
4-Phenyl-1,2,4-triazoline-3,5-dione, a cyclic azo compound with high π acidity, reacted readily with **1** upon mixing in benzene to give an air-stable yellowish precipitate, mp 283–285°, for which the structure shown in eq 5 was deduced from the ir (ν_OH 3490, 3440 cm⁻¹; ν_CO,C=N 1720, 1630 cm⁻¹) and nmr spectra (δ ppm (TMS) 9.47 OH, 5.86 C₅H₅, 7.2–7.5 C₆H₅). Acidic character of the hydroxylic group is revealed by its solubility in aqueous alkali and also by the ¹H nmr chemical shift values (δ 9.47 in DMSO-d₆). Due to its
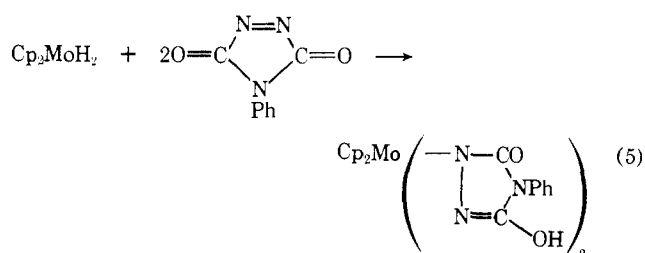

extremely low vapor pressure, the mass spectrum showed no molecular ion peak. An alternative structure with a Mo–O bond
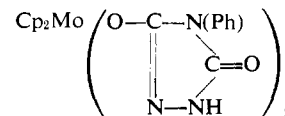
is rejected by the observed ir bands at 3490 and 3440 cm⁻¹ which are most probably due to ν_OH and not to ν_NH, since ν_NH of related diacylhydrazines, phenylurazoles, or acylhydrazones are at ∼3200 cm⁻¹.

In contrast to the transition metal catalyzed decomposition of diazoalkanes, **1** forms a thermally stable complex with diazofluorene, without nitrogen elimination. The elemental analysis and ¹H nmr data determine its composition as Cp₂Mo(C₁₃H₈N₂). The bonding can be inferred from the ir spectrum which shows a strong new band at 1510 cm⁻¹ ascribable to
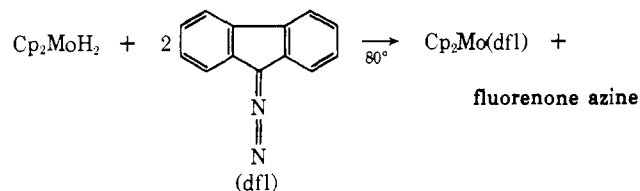
the vibration of the C=N=N group coordinated in a side-on manner. A similar strong band (1480–1520 cm⁻¹) is also found for various nickel(0) or palladium-(0) diazoalkane complexes, e.g., L₂M(dfl) (dfl = diazofluorene).⁶ The exact bonding situation awaits X-ray analysis now under way.

Methyl diazoacetate reacts with **1** through nitrogen elimination only on refluxing in THF. No pure complexes, however, have been isolated so far. A similar reaction with **2** in refluxing THF resulted in recovery of the starting materials. Diazomethane did not react with **1** at room temperature in an ether solution.

Discussion

Bonding in Cp₂Mo(PhN=NPh). Nature of interaction of molybdenum with azo (–N=N–) bonding is interesting in connection with the well-known dinitrogen reducing property of some molybdenum complexes. In particular, the bonding with the Cp₂Mo moiety is closely connected with its ability to form an unstable dinitrogen complex, Cp₂MoN≡N, as recently shown by Thomas and Brintzinger.⁵ Side-on coordination of *trans*-azobenzene to the Cp₂Mo moiety is similar to the bonding in the olefin complexes such as Cp₂Mo(CH₂=CHCN).² When the π acidity⁷ of *trans*-azobenzene and the donor property of Cp₂MH₂ (M = Mo, W) are considered, an extensive delocalization of metal electrons into azobenzene is expected. The ¹H nmr spectrum provides evidence for this. Thus, the Cp protons are deshielded (δ ∼4.80 ppm) as compared with those in Cp₂Mo(PhC≡CPh) (4.45 ppm).² The phenyl protons are more shielded (δ 6.2–7.0 ppm) than the parent azobenzene (δ 7–8 ppm). Ligand exchange studies with other π-acids such as (≡CCO₂CH₃)₂ or O₂ show inertness of the azobenzene complex. Consistently, the mass spectrum shows the strong molecular ion peak. The combined evidence suggests the three-membered ring structure shown below representing the most probable limiting structure.
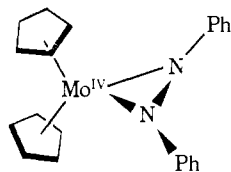
In view of the extreme air sensitivity and ease of ligand exchange of the related nickel–azobenzene complexes, $L_2Ni(PhN=NPh)$, $L = t\text{-}BuNC^7$ and $PPh_3,^8$ the observed air stability and inertness of the molybdenum analog is remarkable. A moderate ionicity of the Mo–N bonds, which reduces the electron density of the filled nonbonding metal orbital, results in inertness to an attack of various π-acids. The partially ionic bond is compatible with the representation of the complex as a Mo(IV) species.

The absence of ortho metalation in the reaction forming **3** implies a quite different mode of the interaction of azobenzene from that observed[17] with $PdCl_2$ or $CH_3Mn(CO)_5$ where electrophilic or nucleophilic aromatic substitution, respectively, is involved. The difference in mechanism may be traced back to the initial interactions between azobenzene and the metal complexes. Thus, the π orbitals of azobenzene interact with "Cp_2Mo" or Ni(0), whereas the lone pair orbital interacts with $PdCl_2$.
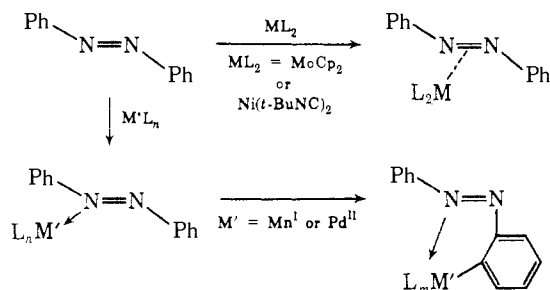

Hydrido–Hydrazino Complexes and Metalloheterocycles.

The enhanced stability of $Cp_2MoH[N(CO_2R)NHCO_2R]$ must be due to the metal electron delocalization into the alkoxycarbonyl group, as supported by the chemical shift values of the Cp protons and the ir C=O stretching frequencies. The isolated hydrido–hydrazino complex constitutes the first example of a stabilized intermediate in metal hydride reduction of diimide or azo compounds into hydrazines. Either concerted 1,2 or 1,4 addition of the Mo–H bond to the $-N=NC=O$ system might be possible for the reaction of **1** with azodibenzoyl or with azodicarboxylates. The 1,4-addition product may also give the hydrazino complex via prototropy (cf. eq 6). As a test for the

(6)
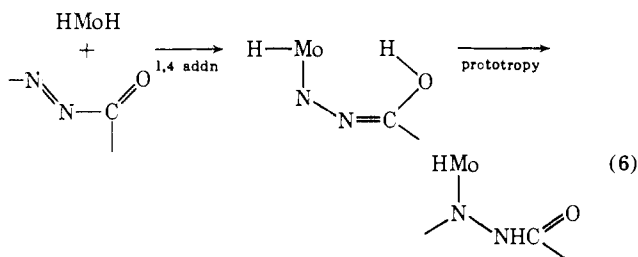
1,4-addition mechanism, a similar reaction was examined with a cyclic carbonyl azo compound, e.g., 4-phenyl-1,2,4-triazoline-3,5-dione, where the concerted 1,4 addition is impossible. The reaction with **1** oc-

curred with comparable ease as for the reaction with azodibenzoyl and gave a product which resulted by primary 1,2 addition to $-N=N-$ followed by prototropy.

(7)
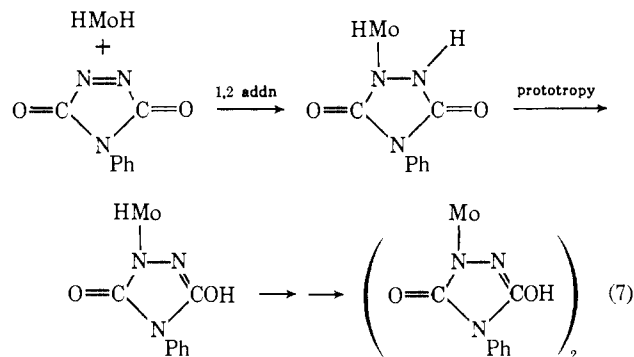
In an attempt to isolate the hydrido–hydrazino intermediate, the 1:1 stoichiometric reaction was tried by addition of the triazolinedione into a benzene solution of **1**. The mixture gave the bis adduct as a precipitate in 18 hr and **1** was recovered unchanged from the solution by sublimation. Insolubility of the bis adduct may shift the equilibrium to the final products.

It is also interesting that simultaneous transfer of two geminal hydrogens on the metal did not take place even though the geometry is favorable. Similar simultaneous transfer has not been observed with olefins or acetylenes.[2]

The formation of the bis-insertion complex from the dihydride **1** has never been observed in the reaction of **1** with olefins or acetylenes. The very strong π acidity of the azo compound coupled with the stability of the $HMo[\sigma\text{-}NCON(Ph)C(OH)=N]$ system probably causes the bis insertion before the thermal decomposition of the system to a hydrazine, $HNNHCON(Ph)C=O$, and Cp_2Mo.

The hydrido–hydrazino complexes (**4**) formed from the azodicarboxylates thermally decompose at $\sim70°$ to give a reactive species, Cp_2Mo, which reacts with an excess of the azodicarboxylate to give a new metalloheterocycle, **5** (cf. eq 3). The reaction with azodibenzoyl proceeds even at room temperature to the corresponding metalloheterocycle **6** (cf. Scheme I). Here, the intermediate hydrido–hydrazino complexes, $Cp_2MH[N(COPh)NHCOPh]$, seem to be less stable.

Although simple side-on addition[7] of an azo linkage ($-N=N-$) to the reactive Cp_2Mo is expected, the reaction with azodicarboxylate or with azodibenzoyl unexpectedly gave novel 1,4 adducts, $Cp_2MN(COR)N=C(R)O$ ($R = OMe$, OEt, Ph). By contrast, only 1,2 adducts (side-on coordination) have been observed for α,β-unsaturated esters,[2] e.g., methyl acrylate. The difference can be attributed to the electron delocalization in the metalloheterocycles, $MNN=CO$. Chemical inertness of these adducts is remarkable. For example, all our attempts to hydrolyze the ester (see Experimental Section) group have been fruitless so far. The thermal and air stability as well as its resistance to light are unusually high. The heterocycles are characterized with the strong electron accepting ability. Deshielding of the Cp protons (δ (TMS) 5.0–5.5 ppm) in comparison with the known alkyl or olefin complexes,[2] e.g., $Cp_2MoH[CH(CH_3)CO_2CH_3]$ or $Cp_2Mo(CH_2=$

CHCO₂CH₃) (δ (TMS) 4.3–4.7 ppm), supports the strong d_π–p_π interactions. The generality and ease of preparation together with the stability of the present metalloheterocycles may open novel aspects in the field of heterocyclic compounds.

Experimental Section

The materials and the apparatus used were described previously.[2] cis-Azobenzene,[20] azomethane,[12,21] dimethyl and diethyl azodicarboxylates,[22] azodibenzoyl,[23] 4-phenyl-1,2,4-triazoline-2,4-dione,[24] and diazofluorene[25] were prepared according to literature. All operations and measurements involving air-sensitive organometallic compounds were performed under pure nitrogen.

Cp₂Mo(PhN=NPh). A reaction mixture containing 1 (450 mg, 1.97 mmol) and trans-azobenzene (717 mg, 3.94 mmol) in tetrahydrofuran (THF) (15 ml) was refluxed for 6 hr. The deep red solution was evaporated and the residue was sublimed to remove a mixture (230 mg) of hydrazobenzene and azobenzene. The sublimation residue (715 mg) was dissolved in tetrahydrofuran and the deep red solution yielded the azobenzene complex (570 mg, 71% yield) as a well-formed crystal after addition of some ether followed by chilling at −20°. The complex reacted readily with excess iodine in chloroform at room temperature to give a greenish brown suspension. Removal of the solvent and extraction with benzene followed by alumina column chromatography gave azobenzene in 64% yield as identified by its melting point and ir spectrum.

Cp₂MoH[N(CO₂C₂H₅)NHCO₂C₂H₅]. Diethyl azodicarboxylate (100 mg, 0.57 mmol) was dropped into a solution of 1 (128 mg, 0.56 mmol) in ethanol (10 ml) at room temperature with stirring. The color turned reddish orange. After being stirred for 6 hr, the reaction mixture was chilled to −20° to give a yellow powdery precipitate which was purified by recrystallization from CH₂Cl₂.

Cp₂Mo[(CO₂CH₃)NNCO₂CH₃]. A THF solution (10 ml) of dimethyl azodicarboxylate (290 mg, 2.0 mmol) was slowly added to a THF solution (10 ml) of 1 (228 mg, 1.0 mmol) at room temperature. The mixture was refluxed for 1 hr to give a dark brown turbid solution. After partial evaporation of the solvent in vacuo followed by chilling to ensure maximal precipitation, the powdery product was washed twice with benzene (10 ml each). The crude product (200 mg), which contains a considerable amount of (NH-CO₂CH₃)₂, was purified by recrystallization from methanol (3 ml). Yellowish brown powder (40 mg), which was obtained after concentration of the methanol solution followed by chilling and thorough washing with toluene, had satisfactory analytical results. Well-formed microcrystals may be obtained by very slow evaporation of the methanol–toluene solution at room temperature.

Cp₂Mo[(CO₂C₂H₅)NNCO₂C₂H₅]. A THF solution (10 ml) of diethyl azodicarboxylate (810 mg, 4 mmol) was dropped into a THF solution (10 ml) of 1 (456 mg, 2 mmol) at room temperature. An instant color change to reddish brown occurred. The reaction mixture was refluxed for 1 hr to give a dark brown turbid solution which was concentrated and chilled to −20°. The brown precipitate was washed with cold benzene and redissolved in hot benzene (at 60°). The filtered benzene solution gave reddish brown fine crystals on partial evaporation and cooling. These crystals were washed well with warm benzene or toluene to give an analytically pure sample (110 mg, 14% yield): λmax (H₂O) 355 nm (ε 2260), (0.1 N Cl) 329 (ε 2320), (0.25 N NaOH) 349 (ε 2400). Evaporation of the mother liquor followed by sublimation gave N,N′-dicarboethoxyhydrazine (mp 131°).

The complex was inert toward aqueous acids or alkalis at room temperature. Attempts to hydrolyze the ester function by use of alcoholic KOH failed even after long refluxing.

Cp₂Mo[(COPh)NNCOPh]. A benzene solution (20 ml) of freshly prepared azodibenzoyl (511 mg, 2.14 mmol) was added at room temperature to a benzene solution (10 ml) of 1 (244 mg, 1.07 mmol) with stirring. The color turned reddish brown and an almost colorless precipitate formed. After stirring for 3 hr, the precipitate was removed by filtration and identified as dibenzoyl-

hydrazine. The filtrate was concentrated to ca. one-tenth volume and allowed to stand overnight to give brownish orange microcrystals (225 mg, yield 45%) which are analytically pure. Further crops may be obtained from the mother liquor: λmax (EtOH) 302 nm (ε 9300) 390 (shoulder); (0.1 N HCl) 317 (shoulder) (ε 10,000); mol wt (CH₂Cl₂) 466, calcd 464.4.

Protonation of Cp₂Mo[(COPh)NNCOPh]. The complex (50 mg) was dissolved in concentrated hydrochloric acid (0.5 ml) at room temperature and the solution was allowed to stand for about 1 hr to precipitate reddish brown crystals. Elemental analysis indicated its formulation as Cp₂Mo[(COPh)NNCOPh]·HCl·3H₂O. Anal. Calcd for C₂₄H₂₇N₂O₅ClMo: C, 51.95; H, 4.91; N, 5.05; Cl, 6.39. Found: C, 51.92; H, 4.35; N, 5.14; Cl, 6.52. Ir (Nujol), 3500, 3300, 3320, 3100 (νOH,NH), 1654, 1626, 1604 (δOH), 1580 (νC=O), 1555 cm⁻¹ (νC=N). ¹H nmr (DCl) δ (ppm, TMS as external standard), 6.35, 6.65 (Cp); 7.9, 8.05, 8.2 (Ph). ¹H nmr in concentrated HCl showed an absence of peaks at the metal hydride region (δ −5 to −15 ppm). When a more dilute solution of the parent complex in concentrated hydrochloric acid was allowed to stand for 1 day, dark brown well-formed crystals (pale green when powdered) formed. Elemental analysis indicated its composition as Cp₂MoCl₂ and the ir spectrum indicated its identity with the authentic sample (νMoCl 390 cm⁻¹) prepared from 1 and CCl₄. A very dilute saturated solution of Cp₂-MoCl₂ in DCl–D₂O exhibited a singlet resonance at δ 6.18 (ppm, external TMS). The solubility and the chemical shift value indicate its absence in a fresh protonation mixture of Cp₂Mo[(COPh)-NNCOPh] in concentrated DCl. Anal. Calcd for C₁₀H₁₀Cl₂Mo: C, 40.43; H, 3.39. Found: C, 40.71; H, 3.34.

Cp₂W[(COPh)NNCOPh]. A benzene solution (20 ml) of freshly prepared azodibenzoyl (492 mg, 2.06 mmol) was added at room temperature to a benzene solution (15 ml) of 2 (325 mg, 1.03 mmol) with stirring. An off-white precipitate formed immediately and the color turned reddish brown. After stirring overnight the precipitate was removed by filtration and identified as dibenzoylhydrazine. The filtrate was concentrated to ca. one-tenth volume and allowed to stand for a few hours to give brownish orange microcrystals. After removal of the mother liquor, microcrystals were well washed with benzene to give an analytically pure sample (145 mg, yield 25%).

Cp₂Mo(dfl). A benzene solution (10 ml) of 1 (225 mg, 1.0 mmol) was mixed with 9-diazofluorene (dfl) (380 mg, 1.98 mmol) in benzene (15 ml) at room temperature. The color slowly turned dark red in 2 hr, but, as the reaction proceeded only a little, the mixture was refluxed for 2 hr to result in a formation of a dark turbid solution. After concentration of the solvent, the turbid solution precipitated dark red powder identified as essentially fluorenoneazine. The mother liquor was mixed with some n-hexane and chilled at −20° overnight to give dark red needles, mp (in air) 84° dec, recrystallized from cold toluene by chilling down to −20°. The analytically pure crystals (mp (N₂) 111–114°, ca. 100 mg) were almost insoluble in n-hexane or methanol but moderately soluble in aromatic solvents. The orange solution was air sensitive, decomposing in air during a few hours at room temperature. Anal. Calcd for C₂₃H₁₉N₂Mo: C, 65.88; H, 4.57; N, 6.68. Found: C, 66.17; H, 4.46; N, 6.54. Cryoscopic measurement of the molecular weight was hampered by its restricted solubility in cold benzene. The mass spectrum could not be measured owing to its low vapor pressure: ¹H nmr (C₆D₆), δ (ppm TMS), 4.30 (s, 10 H, Cp protons), 7.47 and 8.15 (m, 8 H, aromatic protons); ir (Nujol) 1510 cm⁻¹ (diazoalkane coordinated to a metal).[6]

Cp₂Mo[NN=C(OH)N(Ph)CO]₂. 4-Phenyl-1,2,4-triazoline-3,5-

dione (200 mg, 1.2 mmol) was added with stirring to a benzene solution (30 ml) of 1 (131 mg, 0.6 mmol) at 20°. The pale yellow powder soon precipitated. After stirring the reaction mixture for 15 hr, the pale yellow precipitate was separated and evaporated in vacuo. The pale yellow powder was dissolved in dimethyl sulfoxide (ca. 20 ml) and then methanol was added to the filtered solution giving well-formed reddish brown analytically pure crystals (40% yield) insoluble in benzene or CH₂Cl₂.

In a similar manner, a benzene solution of the triazolinedione was dropped into a benzene solution of 1 in a molar ratio of 1:1 at 20°. Yellow precipitates formed in 18 hr and were filtered, washed, and recrystallized to give the same product (yield 45%, identified by melting point, ir, and analysis) as obtained in the above reaction with a 2:1 mole ratio. 1 was recovered in 25% yield from the filtrate by sublimation at 120° (2 mm).

Mass Spectra. For the sake of brevity, a convention described in our previous paper[2] is used. The data are listed in order of

(20) A. H. Cook, J. Chem. Soc., 876 (1938).
(21) J. Thiele, Ber., 42, 2576 (1909).
(22) N. Rabjohn, Organic Syntheses, Coll. Vol. 3, 375 (1955).
(23) T. Imamoto and Y. Yukawa, J. Syn. Org. Chem., 30, 665 (1972).
(24) R. C. Cookson, S. S. Gupta, I. D. R. Stevens, and C. T. Watts, Org. Syn., 51, 121 (1971).
(25) W. Kirmse, L. Horner, and H. Hoffmann, Justus Liebigs Ann. Chem., 614, 19 (1958).

oven temperature, m/e value, relative abundance in parentheses, and probable assignment: $Cp_2Mo(PhN=NPh)$ 130°, 408 (10) M^+, 226 (40) Cp_2Mo, 184 (43) $PhNHNHPh$, 182 (14) $PhN=NPh$, 97 (42) $C_5H_5N_2H_4$, 93 (45) $C_5H_5N_2$, 92 (38) $PhNH_2$, 77 (100) Ph, 71 (62) C_5H_{11}, 69 (61) C_5H_9, 57 (90) C_4H_9; $Cp_2Mo[(CO_2CH_3)NNCO_2CH_3]$ 210°, 372 (30) M^+, 328 (1) $M^+ - CO_2$, 268 (2) Cp_2Mo-NCO, 257 (2) Cp_2MoOCH_3, 240 (4) Cp_2MoN, 226 (100) Cp_2Mo, 116 (22) $C_3H_4N_2O_3$, 103 (51) CH_3NH-NCO_2CH_3, 102 (45) CH_3N_2-CO_2CH_3, 75 (50) $NH_2CO_2CH_3$, 65 (10) C_5H_5, 59 (72) CO_2CH_3;

$Cp_2Mo[(CO_2C_2H_5)NNCO_2C_2H_5]$ 190°, 400 (23) M^+, 356 (1) $M^+ - CO_2$, 328 (1) $Cp_2Mo(CH_3)(CO_2CH_3)$, 268–269 (1) $Cp_2Mo(NCO$ and $NCOH)$, 256–257 (1) Cp_2MoOCH_{2-3}, 240 (3) Cp_2MoN or Cp_2MoCH_2, 226 (65) Cp_2Mo, 104 (23) $NH_2NHCO_2C_2H_5$, 92 (68) C_7H_8, 91 (100) C_7H_7, 78 (68) C_6H_6, 65 (15) C_5H_5.

New 13-Atom Bimetallocarboranes Prepared by Polyhedral Subrogation
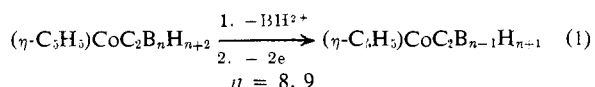
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Contribution No. 3252 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received December 17, 1973

Abstract: The reaction of 13-vertex cobaltacarboranes, $(\eta-C_5H_5)CoC_2B_{10}H_{12}$, with ethanolic potassium hydroxide in the presence of cyclopentadiene and an appropriate metal salt produces new 13-vertex bimetallocarboranes. These bimetallic products, which may contain identical or dissimilar metals, have one less boron atom than does the original monometallocarborane. The preparation, characterization, and structures of these complexes are discussed.

We have recently reported[1,2] an extension of the polyhedral contraction reaction[3,4] in which $4-(\eta-C_5H_5)-4-Co-1,8-C_2B_{10}H_{12}$[5,6] was degraded in the presence of ethanolic potassium hydroxide to form the $[3-(\eta-C_5H_5)-3-Co-4-CB_7H_8]^-$ anion.[7] In an effort to learn more about the mechanism of this unusual reaction, we began a study of some of the side products that were isolated. Among these side products were metallocarboranes of unexpectedly high molecular weight suggesting that the metallocarborane frameworks contained more than one transition metal atom. It thus appeared that the polyhedral contraction reaction, or a modification thereof, might be useful in the preparation of polymetallocarboranes.

The polyhedral contraction process converts certain cobaltacarboranes to their next smaller homolog by the removal of a formal BH^{2+} unit from the polyhedral framework by base degradation followed by a two-electron oxidation (eq 1). If the degradation reaction

$$(\eta-C_5H_5)CoC_2B_nH_{n+2} \xrightarrow[\text{2. } - 2e]{\text{1. } -BH^{2+}} (\eta-C_5H_5)CoC_2B_{n-1}H_{n+1} \quad (1)$$
$$n = 8, 9$$

takes place in the presence of excess metal ion, that metal ion may be inserted into the hole left by the departing boron atom in the polyhedral framework. We have termed this replacement of a boron atom by a metal atom the "polyhedral subrogation" reaction.[8] The reaction itself is not a new one. In fact, the first metallocarboranes were prepared by the removal of a BH^{2+} unit from $1,2-C_2B_{10}H_{12}$ followed by the insertion of an appropriate metal atom.[9] What was once a three-step procedure (eq 2) has recently[10] been con-

$$1,2-C_2B_{10}H_{12} \xrightarrow[C_2H_5OH]{KOH} 1,2-C_2B_9H_{12}^- \xrightarrow{NaH} 1,2-C_2B_9H_{11}^{2-} \xrightarrow[C_5H_5^-]{M^{n+}}$$
$$3-(\eta-C_5H_5)-3-M-1,2-C_2B_9H_{11} \quad (2)$$

densed into a one-step process (eq 3). A procedure

$$1,2-C_2B_{10}H_{12} \xrightarrow[CH_3OH]{KOH, M^{n+}, C_5H_6} 3-(\eta-C_5H_5)-3-M-1,2-C_2B_9H_{11} \quad (3)$$

similar to that shown in eq 3 was used independently by two groups to prepare the icosahedral complex $3,6-(\eta-C_5H_5)_2-3,6-Co_2-1,2-C_2B_8H_{10}$[10,11] and the heterobimetallocarborane $4,5-(\eta-C_5H_5)_2-4-Co-5-Fe-1,8-C_2B_9H_{11}$.[12] We now wish to report the syntheses of additional 13-vertex bimetallocarboranes and one trimetallic species each of which was prepared by the polyhedral subrogation reaction.

Results

The Preparation and Characterization of Homobimetallocarboranes Containing Cobalt. The polyhedral

(1) D. F. Dustin and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1329 (1972).

(2) D. F. Dustin and M. F. Hawthorne, *Inorg. Chem.*, **12**, 1380 (1973).

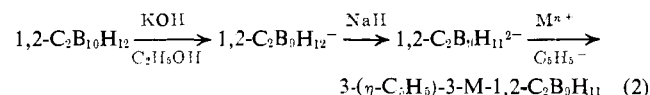(3) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 900 (1972).

(4) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 8391 (1972).

(5) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 3085 (1974).
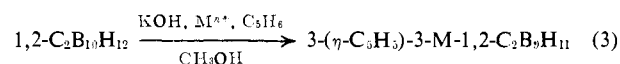
(6) Numbers accompanying formulas refer to the positions of the heteroatoms within the closo metallocarborane framework and to the positions of the exopolyhedral substituents, if any. Lowest numbers consistent with the molecular geometry are given to carbon in accordance with the inverse periodic order adhered to by the IUPAC Inorganic Nomenclature Committee; see R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972). For example, in $4-(\eta-C_5H_5)-4-Co-1,8-C_2B_{10}H_{12}$, cobalt occupies position 4 while the carbon atoms are located at vertices 1 and 8. The cyclopentadienyl ring is π-bonded to the cobalt.

(7) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, in press.

(8) We have chosen the word "subrogation" rather than "substitution" so as not to confuse this reaction with those involving exopolyhedral substitution.

(9) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

(10) J. Plesek, B. Štíbr, and S. Heřmánek, *Syn. Inorg. Metal-Org. Chem.*, **3**, 291 (1973).

(11) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, **12**, 608 (1973).

(12) D. F. Dustin, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 805 (1973).