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Reactions of Transition Metal Dihydrides. VII. Further Investigations on Charge-Transfer Interaction between σ-Basic Metal Hydrides and Organic π-Acceptors

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Charge transfer (CT) absorptions between transition metal polyhydrides, *e.g.* MH_2Cp_2 (Cp=η-C_5H_5; M=Mo, W), $FeH_2(dppe)_2$, $MH_4(dppe)_2$(dppe=$Ph_2PCH_2CH_2PPh_2$; M=Mo, W), and organic π-acceptors such as maleic anhydride were measured. The position of the CT bands gave an I_p value of 6.3 eV for WH_2Cp_2. The value indicates transfer of electron from the filled non-bonding metal orbital to the acceptors. Role of the electron donor-acceptor interactions prior to insertion or substitution of transition metal hydrides is discussed.

Electron transfer reactions of transition metal complexes are receiving considerable attention in modern inorganic chemistry.[1] In many cases, the transfer of electron accompanies a change in formal oxidation state of the metal. In some cases partial transfer of an electron (electron donor accepter interaction or charge transfer) can be observed between metal compounds and organic substances. Our primary concern here is with the intermolecular charge transfer (CT) interactions. Thus, ferrocene forms a green CT-complex[2] with TCNE, whereas cobaltocene ($CoCp_2$ Cp: η-C_5H_5) and nickelocene ($NiCp_2$) give ionic salts, *e.g.* $(Cp_2M)^+(TCNE)^-$, resulting from complete electron transfer.[3] An X-ray structure of the ferrocene/TCNE adduct[4] revealed the charge transfer between the Cp ring and π-orbital of TCNE. A similar structure has been reported for CT complexes of arenechromium tricarbonyls with 1,3,5-trinitrobenzene.[5] H. Kobayashi *et al.* have proposed participation of a metal orbital in the charge transfer observed in arenechromium tricarbonyl/TCNE[6] systems. The ease of electron transfer, in principle, depends on the relative energy levels and electronic configuration of the metal orbitals of these organometallic complexes and on those of the accepting orbitals of organic molecules. This electron donor-acceptor interaction is generally an unobservable low-evergy process, occurring prior to such reactions as olefin π-complex formation and olefin insertion, both of which constitute essential steps in olefin catalysis.

We have been interested in the electron-donating property of various transition metal hydrides and phosphine complexes as they are important in olefin catalysis or organic synthesis in general. During studies on the reactivity of MH_2Cp_2 compounds (M=Mo, W; Cp=η^5-C_5H_5) we were able to observe CT interactions between these metal σ-bases and organic π-acids, and found that the interactions could be influential for the kinetic behavior observed in the subsequent olefin insertion reactions.[7] In addition, this has an important bearing on the olefin catalysis. The absence of study experimentally identifying interactions of this type prompted us to report our study which shed light on the nature of the interactions.

Results

Charge Transfer Complexes. When a concentrated solution of metallocene hydrides, MH_2Cp_2 (M=Mo and W), in toluene or acetonitrile, was mixed with π-acidic olefins such as maleic anhydride or fumaronitrile, immediate coloration, ranging blue to red, occurred. The color is due to the charge transfer absorption band as shown by a trend in the absorption maximum observed when the π-acidity is systematically varied (Table 1). It is important to exclude air from the interacting systems to successfully record the spectra. In many cases, the coloration fades on standing even under nitrogen for *ca.* 1 h. The extreme air-sensitivity of the hydrides and the weakness of the charge transfer absorption made quantitative spectral measurements very difficult. Therefore, no attempt was made to estimate the formation constants of the charge transfer complexes.

The charge transfer bands observed with *N,N*-dimethylaniline, a typical organic donor, are also listed in Table 1 to facilitate the comparison with the data of the metal σ-donor, WH_2Cp_2. An essentially constant shift (≈7000 cm^{-1}) in the maxima is apparent by comparing *N,N*-dimethylaniline with WH_2Cp_2. Hence WH_2Cp_2 has a lower I_p than that of dimethylaniline. Since the I_p of the dimethylaniline is 7.1 eV,[8] the I_p value for WH_2Cp_2 will be 6.3 eV. The estimated I_p value is in good agreement with the I_p data obtained by an ESCA[9] (6.4 eV), and by an photocurrent measurement[10] (6.3±0.1 eV), but different from one by a molecular orbital calculation (8.3 eV).[11]

The variation of polarity of the solvent from CH_2Cl_2 to benzene caused a moderate blue shift (20000 cm^{-1} to 19200 cm^{-1}) of the maxima of charge transfer band for the system WH_2Cp_2/citraconic anhydride. The approximate value of the extinction coefficient (ε: 5×10^3) in neat citraconic anhydride was as expected for the charge transfer absorption. These characteristics of the spectra unambiguously indicate the absorption maxima to be real charge transfer band.

Substitution with a methyl group on the Cp rings in MH_2Cp_2 molecule did not significantly affect the band. Thus, $WH_2(C_5H_4CH_3)_2$[12] exhibited a blue color (λ_{max} at 528 nm) in neat citraconic anhydride. MoH_2Cp_2 and $MoH_2(C_5H_4CH_3)_2$[12] exhibited almost the same pale blue color when mixed with phenylmaleic anhydride in toluene. The color turned to deep brown in 1 h at room temperature. In comparison with the tungsten congener, the molybdenum hydride, MoH_2Cp_2, did not show a clear absorption maximum even with maleo- or fumaronitrile in toluene. The coloration is very similar to the case with the tungsten hydride. The similarity

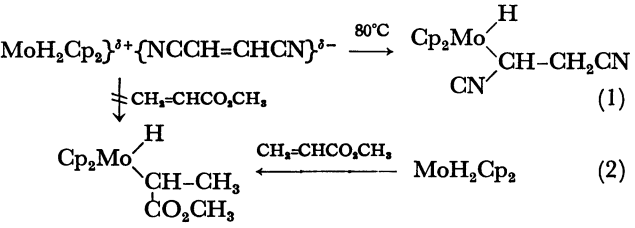
TABLE 1. FREQUENCIES OF CHARGE TRANSFER BANDS

Acceptor	Donor Cp_2WH_2[a)]		Donor $PhN(CH_3)_2$	
	Color	Maximum ($10^3 \times cm^{-1}$)	Color	Maximum ($10^3 \times cm^{-1}$)
Phenylmaleic anhydride	Blue	15.8	Red orange	22.6
Maleic anhydride	Bluish violet	17.5	Reddish orange	24.6
Methylmaleic anhydride (citraconic anhydride)	Purple	19.2	Orange	26.2
Dimethylmaleic anhydride	Reddish purple	20.0[b)]	Orange	27.2
Nitrobenzene	Red	20.0	Yellow	—
m-Dinitrobenzene	Pale violet	17.8	Orange	23.8
1,3,5-Trinitrobenzene	Pale blue	16.8[b),c)]	Red	20.6
Dimethyl maleate	Red	25.0[b)]	—	—
Dimethyl fumarate	Red	22.5[b)]	—	—
Fumaronitrile	Deep red	20.0[b)]	Yellow	27.0
Maleonitrile	Deep red	20.0[b)]	Yellow	27.0
Tetracyanoethylene	Ionized complex (Brown)		Blue	14.6

a) 0.002—0.01 mol/l for WH_2Cp_2 as donor. b) Shoulder. c) Inaccurate due to faint absorption.

indicates that the I_p value[9)] for MoH_2Cp_2 is essentially identical to WH_2Cp_2. The failure to observe clear maxima for MoH_2Cp_2/π-acceptor systems may be due to the instability of the hydride $[MoH_2Cp_2]^{\delta+}$ with partial positive charge in solution. Although trihydrido cation, $[MoH_3Cp_2]^+$, is coordinatively saturated and thermally stable, the dihydrido cation, $[MoH_2Cp_2]^+$, is thermally unstable as evidenced by reaction between MoH_2Cp_2 and TCNE as described below. Generally tungsten hydride complexes are much more inert to olefins than the corresponding molybdenum hydride complexes.[12)]

Although formation constants of the CT complexes of metallocene hydrides have not been measured, the intensity of the coloration implies that the values are low. Small formation constants have been recorded in systems such as polypermethylsilane/TCNE.[13)] Due to the small formation constants, we could not measure the exact absorption maximum, especially with MoH_2Cp_2 as the donor. A faint coloration due to the CT absorption was observed in the following interactions: $MoH_2Cp_2/Ph_2C{=}C(CN)_2$, faint red; MoH_2Cp_2/pyromellitic dianhydride, faint blue (in CH_3CN).



$$\{MoH_2Cp_2\}^{\delta+}\{NCCH{=}CHCN\}^{\delta-} \xrightarrow{80°C} Cp_2Mo(H)[CH(CN){-}CH_2CN] \quad (1)$$

$$\{MoH_2Cp_2\}^{\delta+}\{NCCH{=}CHCN\}^{\delta-} \not\xrightarrow{CH_2{=}CHCO_2CH_3}$$

$$Cp_2Mo(H)[CH(CO_2CH_3){-}CH_3] \xleftarrow{CH_2{=}CHCO_2CH_3} MoH_2Cp_2 \quad (2)$$

The deep red solution of the CT complex, MoH_2Cp_2/fumaronitrile, gave a hydrido-σ-alkyl complex on heating to 80 °C in toluene (Eq. 1). An attempted reaction of the CT complex with methyl acrylate did not give the acrylate insertion product which can be readily prepared by the reaction with MoH_2Cp_2 even at 0 °C (Eq. 2). Similar insertion of fumaronitrile into one of the W–H bonds in $\{WH_2Cp_2\}^{\delta+}\{NCCH{=}CHCN\}^{\delta-}$ did not occur at 80 °C.

The interaction of metallocene monoalkyl–hydrides, *e.g.* $Cp_2MoH[CH(CN)CH_2CN]$ with π-acceptors *e.g.* TCNE, did not give rise to charge transfer absorptions.

A rhenium hydride, $ReHCp_2$, also exhibited a CT maximum with trinitrobenzene at 540 nm and with citraconic anhydride at 480 nm in CH_3CN.

The interaction in mixture of MH_2Cp_2 and π-acceptors was investigated by physical methods such as the infrared and NMR spectroscopy and conductivity measurements. Thus, evaporation of a solution of an equimolar mixture of WH_2Cp_2 and maleonitrile gave a deep red solid which shows a new somewhat broad IR $\nu_{C\equiv N}$ band at 2200 cm^{-1} in addition to the bands due to the free olefin at 2237 and 2256 cm^{-1}. Similarly, evaporation of the solution containing fumaronitrile gives an orange solid which is contaminated by crystals of the starting materials and also shows a new ν_{CN} band at 2200 cm^{-1}. Conductivity measurement of the CT mixture dissolved in CH_2Cl_2 clearly shows some increase in conductivity as compared with the value of each component at the same concentration. The molar conductivity ($\Lambda = 1.0 \times 10^{-3}\ \Omega^{-1}\ cm^2\ mol^{-1}$) suggests presence of solvent-separated ions in small concentrations and yet provides firm evidence for the presence of an intimate ion pair together with the CT complex in the solution.

A similar, but weaker, red coloration was observed for systems, $MoH_2Cp_2/PhCH{=}CHCN$, or $/CH_3CH{=}CHCN$. No physical evidence has been obtained for these weakly interacting systems. The tungsten analog, WH_2Cp_2, behaves similarly to the Mo derivative, but the red coloration is still weaker. The red C_6D_6 solutions of a system, MoH_2Cp_2/maleonitrile or WH_2Cp_2/maleonitrile, were examined by ^1H NMR spectroscopy. The signals observed were almost identical to those of the each component only. These results are in agreement with the small formation constants of the CT complexes. Consistently, the IR spectrum of the concentrated solution showed only a weak peak at 2200 cm^{-1}, in addition to the ν_{CN} of unchanged maleonitrile.

Electron Transfer Complexes. Formation of the ionized species was demonstrated in the reaction of

MH_2Cp_2 with strong π-acids. Thus, tetracyanoethylylene (TCNE) was mixed, at −35 °C in toluene or in CH_2Cl_2, with dilute solutions of MH_2Cp_2 (M=Mo and W) to give deep brown precipitates, soluble only in polar, coordinating solvents. When the components are mixed in high concentrations, evolution of H_2 was observed in small amounts. The composition and the visible spectrum (in DMSO) of the product depend on the reaction conditions. Thus, elemental analysis indicated compositions, $MoH_2Cp_2\cdot(TCNE)_n$, $n=1$—1.5 and $WH_2Cp_2\cdot(TCNE)_n$, $n=1$—1.5. $ReHCp_2$ behaves similarly, and instantly gives brown precipitates from benzene solution. Infrared CN stretching frequencies (2150, 2200 cm^{-1}), visible, and conductivity data (see Experimental) suggest an ionized structure[14) analogues to the known ionic compounds, $Cr(C_6H_6)_2{}^+TCNE^-$.[3) The ^1H NMR spectrum in dimethyl-d_6 sulfoxide exhibited only a broadened signal at δ 5.5 indicating its paramagnetism, but the bulk magnetic moment was not measurable.

Tetracyanoquinodimethane (TCNQ) also gives deep brown precipitates from benzene solutions of MH_2Cp_2. In acetonitrile, the addition of MH_2Cp_2 at first gave a deep red solutions which then became deep green. The visible spectrum (in CH_3CN) indicated the presence of $TCNQ^{\bar{\cdot}}$.[14) The deep green powder obtained by evaporation had a composition, $[WH_2Cp_2\cdot(TCNQ)_2]$ with λ_{max} (in CH_3CN) 780, and 820 nm. 9,10-Phenanthrenequinone when mixed with MH_2Cp_2 (M=Mo, W) in benzene instantly produces deep purple precipitates which revert to the starting materials on dissolution in dimethyl sulfoxide. No coloration due to the CT interaction of WH_2Cp_2 was observed with anthraquinone, azobenzene, or succinic anhydride.

Electron Donor-Acceptor Interactions of Coordinatively Saturated Transition Metal Hydrides. Coordinatively saturated hydride complexes, *e.g.* $MH_4(dppe)_2$ (M=Mo, W, dppe=$Ph_2PCH_2CH_2PPh_2$) or $MH_2(dppe)_2$ (M=Fe, Ru), exhibit σ-basicity towards CF_3CO_2H and also an electron transfer with TCNE or TCNQ in acetonitrile, as evidenced by the visible peaks of $TCNE^{\bar{\cdot}}$ or $TCNQ^{\bar{\cdot}}$. The ratio of donor/acceptor in the interactions were investigated for the $MoH_4(dppe)_2$/TCNE system and found to be 1 : 2 by the visible spectrum. The electric conductivity in CH_3CN was found to be Λ_m= 64 Ω^{-1} cm^2 at ambient temperature. The value for the $MoH_4(dppe)_2$/TCNQ was Λ_m=49 Ω^{-1} cm^2. Strong green coloration was observed when these interactions were examined in benzene or toluene. The band positions in benzene vary with the different donors; *e.g.* $MoH_4(dppe)_2$/TCNE 613 nm, $Mo(N_2)_2(dppe)_2$/TCNE 617 nm, $WH_4(dppe)_2$/TCNE 630 nm (at −30° in toluene), $FeH_2(dppe)_2$/TCNE 639 nm.

The green color due to the CT band of $MoH_4(dppe)_2$/TCNE slowly changed to purple on standing for a day. A deep purple powder obtained by evaporation had a composition near $Mo(TCNE)_2(dppe)_2$ which can be separated by alumina chromatography into at least seven components differing in color. Low-valent phosphine complexes, *e.g.* $CoH(dppe)_2$, $Ni(dppe)_2$, $NiI_2(PPh_3)_2$, and $CoI_2(PPh_3)_2$, transfer an electron to TCNE when mixed in CH_3CN. No CT absorptions have been detectable even in non-polar solvents, such as benzene.

Discussion

Transition metal complexes in low-valent states are readily oxidized by electron transfer when some electron acceptors are allowed to react with it. The one- and two-electron transfer processes have long been important research fields in inorganic chemistry. However, only a few examples has been known for ***charge transfer*** complex formation arising from the non-bonding orbitals of low-valent transition metal compounds (metal donors) to organic acceptors. The paucity of examples for the charge transfer complexes with metal donors seems to be due to the ease of electron transfer from the non-bonding metal orbitals. For example, only very low energy barrier exists to remove one electron from octahedrally coordinated cobalt(II) ions. Our successful observation of a clear charge transfer absorption band for a system, MH_2Cp_2/π-acceptors, can be ascribed to the sufficient energy barrier of Cp_2MH_2 molcules to loose one electron. The charge transferred state is stabilized presumably due to the high potential energy of the positively charged species, $[MH_2Cp_2]^+$. Indeed, the dihydridometallocene cation, formed by addition of TCNE into a benzene solution/suspension of MH_2Cp_2, slowly decomposes with evolution of hydrogen at room temperature. A qualitative energy profile of the processes are schematically shown in Fig. 1.

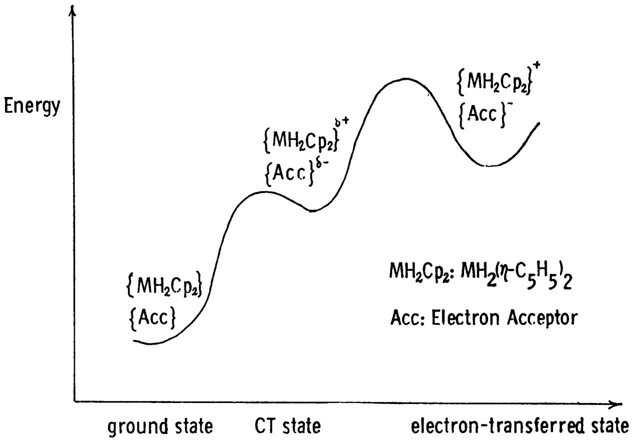


Fig. 1. A qualitative energy profile of the electron transfer process between metallocene dihydrides and electron acceptors.

The relative instability of the cationic species thus seems to be the prerequisite to observe charge transfer states. Some organic electron donors such as *N*,*N*,*N'*,-*N'*-tetramethyl-*p*-phenylenediamine and their derivatives form relatively stable cationic species through one-electron transfer. In contrast to these delocalized electron donors, aliphatic or simple aromatic monoamines do not form stable cationic species but form charge transfer complexes with relevant acceptors.[8) Metallocene hydrides thus resemble these monoamines in their ability to form charge transfer complexes. The present systems represent rare cases where the charge transfer from the essentially non-bonding metal orbital is possible.

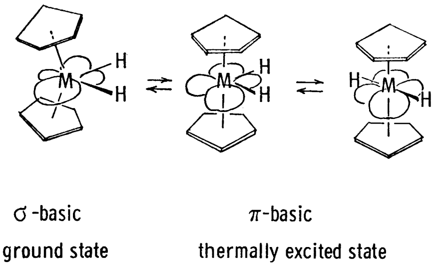
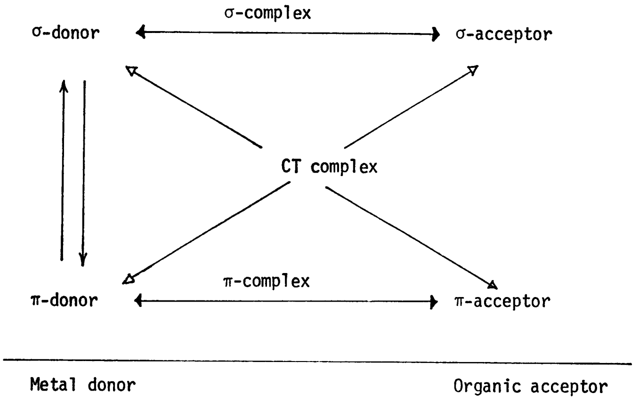


Fig. 2. Shape of an essentially non-bonding metal orbital of $MH_2(\eta\text{-}C_5H_5)_2$ molecules.

The interaction of low-valent transition metal compounds with π-acidic molecules frequently leads to π-complex formation. The propensity for the π-complex formation is especially pronounced with labile low-valent compounds of d^8- of d^{10}-metals, *e.g.* $Pt(PPh_3)_4$. Although the I_p values[15] of these compounds are in a range (6—8 eV) suitable for the charge transfer complex formation with relevant acceptors, no evidence of the charge transfer has been recorded so far. Ligand dissociation from these low-valent compounds affords a metal site of strong π-basicity which rapidly combines with the π-acceptor. Therefore unless ligand substitution process in the donor molecules is prevented either thermodynamically or kinetically, stable charge transfer complexes should not be observable.

WH_2Cp_2 molecule seems to be sufficiently inert to π-complex formation as the shape of the HOMO defines its σ-basic property at the wedged ground-state structure and the π-complex formation with π-accepting olefins is forbidden by the orbital symmetry restriction.[16] In the thermally excited parallel metallocene structure, π-basic property is expected as illustrated in Fig. 2. Thus, thermal reaction of WH_2Cp_2 with diethyl maleate gives $Cp_2W(EtO_2C\text{–}CH\text{=}CH\text{–}CO_2Et)$ through the initial insertion into one of the W–H bonds[17] followed by reductive elimination producing a strong metal π-base, Cp_2W. The insertion has been proposed to proceed *via* incipient π-complex formation with WH_2Cp_2 in the parallel metallocene structure.



Scheme 1. Idealized schemes of interaction between metal donors and organic acceptors.

Scheme 1 shows a simplified scheme for the interactions between metal donors and organic acceptors with an emphasis on the symmetry property of interacting orbitals. It is to be noted that the symmetry properties of the metal donor orbitals will be altered by a change in the stereochemistry or coordination number. The energy barrier for the change generally increases with an increase in the strength of the metal-ligand bonding.[18] In particular, the molybdenum analog of metallocene hydrides, MoH_2Cp_2, undergoes the stereochemical change more readily than the corresponding tungsten complex.[12] In other words, MoH_2Cp_2 is stereochemically more non-rigid than WH_2Cp_2. This trend is in agreement with the general tendency in the non-rigidity of transition metal hydrides[18] and also explains the different behavior of these metallocene hydrides toward electronegative olefins. Thus, MoH_2Cp_2 readily inserts methyl acrylate into one of the Mo–H bonds at 20 °C and the CT complex, MoH_2Cp_2/fumaronitrile, is also slowly transformed to the insertion products (*cf.* Eqs. 1 and 2). By contrast, the tungsten hydride, WH_2Cp_2, forms CT complexes but no insertion products at 20 °C. Since the olefin insertion has been proposed[16] to proceed by incipient formation of a metal-olefin π-complex, the inertness of WH_2Cp_2 seems to be due to its reluctance to undergo polytopal rearrangement to give the thermally-excited π-basic form shown in Fig. 2.

Conclusions

Clear charge transfer absorption maxima were observed for the first time in the interaction of π-basic metallocene hydrides, MH_2Cp_2, with π-acidic organic molecules.[7] The *charge transfer* arises from the filled nonbonding metal orbital as indicated by the substituent effect on the Cp rings of MH_2Cp_2 and also by the I_p value calculated from the charge transfer absorption maxima. *Electron transfer* occurs between MH_2Cp_2 and strong π-acids like TCNE. The formation of charge transfer or electron transfer complexes of MH_2Cp_2 retards the olefin insertion into the M–H bonds. Hence, we feel that these electron-donor-acceptor interactions between metal σ-bases and organic π-acids are not prerequisite to π-complex formation of olefin insertion.

Experimental

Material and Apparatus. Metallocene hydrides (MH_2Cp_2, M=Mo, W and $ReHCp_2$),[19] $MH_4(dppe)_2$ (M=Mo, W),[18] and $MH_2(dppe)_2$ (M=Fe, Ru)[20] were prepared by literature methods. Maleonitrile was prepared from maleamide by dehydration with P_2O_5. The other organic acceptors are commercial products and were purified when necessary. Electronic, vibrational, and ^1H NMR spectra were measured by a Hitachi Model EPS-3T, a Hitachi-Perkin Elmer Model 225, and Jeol JMN-60HL, respectively. Electric conductivity was measured by a Yanagimoto's Conductivity Outfit MY-7 using white platinum plates as electrodes. These physical measurements with air-sensitive metal complexes were performed under pure nitrogen in solvents previously saturated with nitrogen.

Measurement of the Charge Transfer Spectra. Saturated toluene solutions of MH_2Cp_2 (M=W or Mo) were mixed with organic acceptor in question and the supernatant liquor was taken out by a syringe to a 2 mm cell for immediate examination by the visible spectra. When liquid acceptors, *e.g.* maleonitrile or citraconic anhydride, were to be examined, the measurement was also performed in neat liquids. The visible spectra of interacting CT couples, $MH_4(dppe)_2$/TCNE (M=

Mo, W) or $MH_2(dppe)_2$/TCNE (M=Fe, Ru) were recorded similarly in toluene.

Investigation of Physical Property of Interacting Mixtures of MH_2Cp_2 (M=Mo or W) with Fumaro- or Maleonitrile at Ambient Temperature. *a) Visible Spectrum*: An equimolar fresh solution of MoH_2Cp_2 and fumaro- or maleonitrile in dichloromethane (0.1 mmol/l) showed no maximum in the visible absorption. A difference spectrum revealed an increased absorption in the equimolar mixed solution (0.06 mmol/l) at 360—450 nm region without maximum. Experimental difficulty, however, precluded quantitative data. When the amount of fumaronitrile is increased to 2—4 times molar in excess, the absorption around 500 nm increased and when a more concentrated solution (0.1 mol/l) was made, the spectrum began to show a distinct shoulder at 490 nm (ε 10000). By contrast, WH_2Cp_2 showed a clear absorption maximum with many organic acceptors in toluene or in CH_3CN (*cf.* Table 1).

b) Conductivity: Conductivity was measured by a Yanagimoto MY-7 with white platinum electrodes at 1 cm apart, under nitrogen when necessary. A dichloromethane solution (0.1 mmol/l) of MoH_2Cp_2 containing 10-fold excess fumaronitrile showed low molar conductivity, $0.1\times10^{-3}\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 23 °C. Each reagent showed no conductivity in dichloromethane. The result in acetonitrile was complicated by low conductivity of each reagent, but a value $2\times10^{-3}\ \Omega^{-1}\ cm^2\ mol^{-1}$ was found in reddish orange solution made from MoH_2Cp_2 and excess fumaronitrile.

c) ^1H NMR Spectrum: An orange equimolar mixture of MoH_2Cp_2 and fumaro- or maleonitrile freshly dissolved in C_6D_6 or in $(CD_3)_2CO$ failed to give any unambiguous evidence for the formation of an stable adduct as judged from the chemical shift values of the observed peaks, which differ only *ca.* 0.1 ppm from that of free olefins. Similar results were obtained for WH_2Cp_2 as a donor. Observed change in the value from that of the free olefins may indicate difference in extent of solvation because the solvent effect was exceptionally large in C_6D_6.[21] On standing for a few hours at room temperature, weak signals due to the hydride–alkyl complex[16] appear.

d) IR Spectrum: Solution spectra of the fresh mixture of MoH_2Cp_2 or WH_2Cp_2 and fumaronitrile (ν_{CN} at 2246 cm^{-1}) in toluene or in acetone revealed a weak new $\nu_{C\equiv N}$ band at 2200 cm^{-1}. On standing the solution of MoH_2Cp_2 containing fumaronitrile, a strong $\nu_{C\equiv N}$ band (at 2190 cm^{-1}) of the hydrido-alkyl complex appeared.[16] The hydrido-alkyl complex did not form from WH_2Cp_2 even at higher temperatures.

Interaction of MH_2Cp_2 (M=W and Mo) with Tetracyanoethylene (TCNE). Dropwise addition of a dilute TCNE solution in toluene (0.13 g in 10 ml) into WH_2Cp_2 dissolved in toluene (0.03 g in 5 ml) at −35 °C gave a deep purple floculent precipitate which changed to deep brown on further addition. It was filtered, washed, and dried to give a dark brown powder soluble in dimethyl sulfoxide (DMSO) and also in *N*-methylformamide. Attempted purification by recrystallization has been unsuccessful. Elemental analysis roughly corresponded to $WH_2(C_5H_5)_2(C_6N_4)_{1.5}$. IR (Nujol) in cm^{-1}, $\nu_{C\equiv N}$, 2200 broad, 2130 broad, 1600 broad. Visible maxima (DMSO) in nm, 398, 415, 570 shoulder. ^1H NMR spectrum (DMSO-d_6) was obscured by some paramagnetic impurities although the most part was diamagnetic as confirmed by magnetic susceptibility measured in the same solution. The solution had a weak electrolytic property ($\Lambda_m=3.6\ \Omega^{-1}\ cm^2$) in DMSO at 20 °C which somewhat increased on standing. The sample prepared by the inverse addition had similar analytical data but a different visible spectrum (λ_{max} (in nm) at 393, 420 sh, 450 sh). The corresponding reaction of MoH_2Cp_2 with TCNE evolved a small amount of hydrogen, giving a deep brown amorphous powder soluble in DMSO; $[Mo(C_5H_5)_2H_2(C_6N_4)_{1-1.5}]$, IR (Nujol) in cm^{-1}, 2200 broad, 2130 broad, 1650—1600 broad. No maximum was observed in the visible spectrum in DMSO. $\Lambda_m=6\ \Omega^{-1}\ cm^2$ in DMSO at 20 °C. The rhenium hydride, $ReHCp_2$, instantly gave brown precipitates on mixing with a TCNE solution in benzene. The IR spectrum was similar to those obtained by reaction MH_2Cp_2 with TCNE.

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