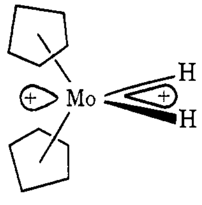
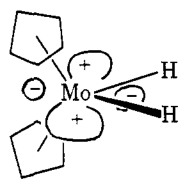
Reaction of Transition Metal Dihydrides. II.[1] Electron Donor–Acceptor Complexes Formed from σ-Basic Complexes Cp_2MH_2 (M = Mo and W) and Their Role in Insertion Reactions

Sir:

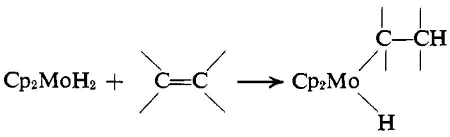
Pronounced Lewis basicity of Cp_2MH_2[2] (Cp = h^5-C_5H_5; M = Mo, W) as exhibited by the formation of σ-donor–acceptor complexes, *e.g.*, $Cp_2MH_2 \cdot AlX_3$, is ascribed to the filled nonbonding orbital. Several hybridization schemes defining the orbital shape (*vide infra*) were proposed[3] for this valency orbital with a common premise of a_1 symmetry. The proposed shapes of the orbital are not suitable for π interaction with π^* orbitals of an olefin or a similar two-center π-acid. Although olefin complexes of formula $Cp_2MH_2(Un)$ (Un = π-coordinated olefin) are unknown, reaction of Cp_2MH_2 with activated olefins (π-acids) occurs leading to the addition across the M–H bond (insertion) (eq 1). It should therefore be of interest to experimentally determine if a charge transfer (CT) interaction takes place prior to the σ-alkylmetal bond formation.



Ballhausen model



Alcock-Green model



$$Cp_2MoH_2 + \;\rangle C{=}C\langle\; \longrightarrow Cp_2Mo\begin{matrix} \diagup \overset{|}{C}-\overset{|}{C}H \\ \diagdown H \end{matrix} \qquad (1)$$

Addition of an excess of maleonitrile to a pale yellow toluene solution of Cp_2MoH_2 (2×10^{-3} mol/l.) at room temperature results in a deep red solution. At this stage, insertion (eq 1) is not occurring since the ^1H nmr signals remain merely a superposition of those of the two components. Upon being heated to 80°, a brown precipitate of the insertion product $Cp_2Mo(H)[CH(CN)CH_2CN]$[1] formed. The incipient formation of an electron-donor–acceptor (EDA) complex can be detected for a number of activated olefins and aromatics by observing the color. Some typical examples of the charge transfer frequencies obtained with Cp_2WH_2 are shown in Table I, which also includes charge transfer frequencies observed with a typical donor, *N,N*-dimethylaniline. Comparison of the absorption maxima between the two donors immediately reveals parallelism; *viz.*, for a series of maleic anhydride, monomethylmaleic anhydride (citraconic anhydride), and dimethylmaleic anhydride, each olefin shows a constant bathochromic shift of ~7000 cm^{-1} from $C_6H_5N(CH_3)_2$ to Cp_2WH_2, implying a lower ionization potential for the organometallic. Fumaronitrile and polynitrobenzenes also show a similar trend. For a system, Cp_2WH_2–citraconic anhydride, a moderate blue shift occurred upon change of solvent from benzene to acetonitrile: ν_{max} (cm^{-1}) 19,200 (C_6H_6), 19,200 (citraconic anhydride), and 20,000 (CH_3CN). The extinction coefficient for the same system was 5×10^3 in neat citraconic anhydride. This is the first reported example of EDA complexes formed between a basic transition metal hydride and olefins.[4] Although some hydride–π-olefin complexes of platinum,[5,6] iridium,[7–9] ruthenium,[10] molybdenum,[11] and niobium[12] are known, EDA complex formation has not been detected so far.

Table I. Maxima of CT Bands in Benzene

Acceptor	Cp_2WH_2[a] Color	Cp_2WH_2[a] Max, cm^{-1}	$C_6H_5N(CH_3)_2$ Color	$C_6H_5N(CH_3)_2$ Max, cm^{-1}
Maleic anhydride	Bluish violet	17,500	Reddish orange	24,600
Citraconic anhydride	Purple	19,200	Orange	26,200
Dimethylmaleic anhydride	Reddish purple	~20,000[b]	Orange	27,200
Fumaronitrile	Red	~20,000[b]	Orange	27,000
m-Dinitrobenzene	Pale violet	17,800	Reddish orange	23,800
1,3,5-Trinitrobenzene	Pale green	~16,800[b,c]	Red	20,600

[a] 0.002–0.01 mmol/l. for Cp_2WH_2 as donor. Measured under nitrogen. [b] Shoulder. [c] Inaccurate due to faint absorption.

Although there is a possibility of participation of the Cp ring in the EDA complex formation as in a ferrocene–TCNE complex,[13] the remarkably enhanced electron donating property of Cp_2WH_2 toward π acceptors compared with ferrocene suggests that the filled metal orbital in wedged metallocenes is more likely to be involved in the charge transfer interaction.

A question then arises as to whether the EDA complex is an intermediate leading to insertion (eq 1). In the case of organic amines the charge transfer interaction with an acceptor leads to products *via* outer and inner complexes ($D^{\delta+} \cdots A^{\delta-}$ and D^+–A^-).[14] β-Cyanoethylation of a primary amine may also involve such charge transfer interactions which are not detected because of rapid σ-bond formation. In contrast we observed a retarding effect of the EDA interaction exerted on the insertion reactions. For ex-

---

(1) For part I, see A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **94**, 1886 (1972).

(2) J. C. Kotz and D. G. Pedrotti, *Organometal. Chem. Rev.*, **4**, 479 (1969); D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970).

(3) J. P. Dahl and C. Ballhausen, *Acta Chem. Scand.*, **15**, 1333 (1961); N. W. Alcock, *J. Chem. Soc. A*, 2001 (1967); J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 421 (1972).

(4) Experimental difficulty inherent to Cp_2WH_2, *i.e.*, high air-sensitivity, limited solubility, and strong absorption above 25,000 cm^{-1}, discouraged measurement of equilibrium constants for EDA complex formation.

(5) A. J. Deeming, B. F. G. Johnson, and J. Lewis, *Chem. Commun.*, 598 (1970).

(6) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **11**, 1275 (1972).

(7) R. W. Haszeldine, R. L. Lunt, and R. V. Parish, *J. Chem. Soc. A*, 3711 (1971).

(8) M. S. Frazer and W. H. Baddley, *J. Organometal. Chem.*, **36**, 377 (1972).

(9) L. M. Haines and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1891 (1972).

(10) J. J. Hough and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 371 (1972).

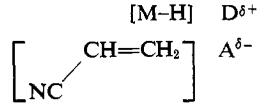
(11) F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organometal. Chem.*, **44**, C13 (1972).

(12) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

(13) E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Amer. Chem. Soc.*, **89**, 4540 (1967).

(14) T. Yamaoka and S. Nagakura, *Bull. Chem. Soc. Jap.*, **44**, 1780 (1970); T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, *ibid.*, **44**, 380 (1971); T. Nogami, K. Yoshihara, and S. Nagakura, *ibid.*, **45**, 122 (1972).

ample, the insertion of methyl acrylate or dimethyl fumarate is complete in 1 hr in toluene at room temperature whereas a higher temperature (80°) is required to effect the insertion with a more acidic olefin, *i.e.*, fumaronitrile or maleic anhydride, indicating lack of a simple correlation between the reaction rate and the π acidity of the olefin components. The insertion of acrylonitrile to Cp_2MoH_2 occurs unexpectedly slowly, leading exclusively to the α-metalated product Cp_2MoH-[$CHCH_3$)CN],[1] in a direction opposite to that of the β-cyanoethylation of amines. Cis stereochemistry of Cp_2MoH_2 addition to disubstituted olefins, implying a multicentered transition state, has been established.[15] Therefore, a similar transition state may be invoked to account for the observed metalation. The direction of the addition implies hydridic character of the hydride ligand of Cp_2MoH_2. However, the partial positive character of $D^{\delta+}$ in the complex would tighten the metal–hydride bond, thus retarding the hydride transfer to the olefin. Kinetic aspects of insertion (eq 1), *inter alia*, the long induction period experienced



by olefins of high π-acidity,[15] also argue against the EDA complex as an activated intermediate. The retarding effect seems to support involvement of essentially metal orbitals in the EDA interaction.

(15) A. Nakamura, Abstracts, 5th International Conference on Organometallic Chemistry, Moscow, 1971, p 555.

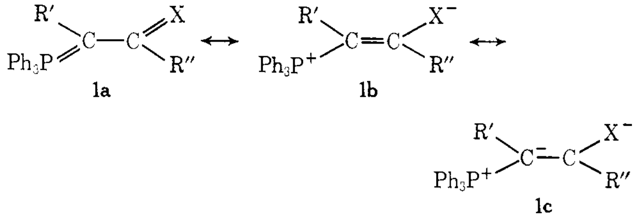
A. Nakamura, Sei Otsuka*
Department of Chemistry, Faculty of Engineering Science
Osaka University, Toyonaka, Osaka, Japan

Received February 27, 1973

^{13}C Nuclear Magnetic Resonance of Organophosphorus Compounds. VII. Probing the Phosphorus–Carbon Ylide Bond

Sir:

Phosphorus ylides have provided challenging problems to both synthetic chemists and those attempting to explain their chemistry and molecular electronic structure.[1] It has been common to interpret their bonding in terms of valence-bond resonance hybrids of the type **1a–c** in explaining their stability,[2] isomerism,[3] and equilibria.[4] The electronic differences within **1a–c** should give rise to fundamental differences in the ^{13}C shieldings and ^{13}C–^{31}P nuclear spin couplings for atoms in the P–C–C–X group for any molecule described largely by one of the above resonance hybrids. Structure **1b** is essentially that of a phosphonium salt, shifts and couplings for which are available in other compounds. Structure **1c** represents a carbanion which could be, in principle, either trigonal or tetrahedral with formal sp^2 or sp^3 hybridization schemes for the ylide carbon. The dπ–pπ "back-bonding" depicted by **1a** presents an electronic distribution for which few ^{13}C data are available.[5]



We have determined ^{13}C–^{31}P couplings and ^{13}C chemical shifts in a number of phosphorus ylides in an effort to better delineate the ylide carbon bonding description. The compounds in Table I were run as received (except for **3** and **6** which were recrystallized from CH_2Cl_2–$(C_2H_5)_2O$ and dried) from Aldrich Chemical Co. in saturated deuteriochloroform solution (usually 250–750 mg/ml) containing 1–5% tetramethylsilane as reference. Solutions were examined in 12-mm tubes using a Varian XL-100-15 nmr spectrometer in Fourier transform mode. Several hundred to several thousand transients were accumulated typically with acquisition times of 1.0–3.3 sec with 1.7 sec being normal for coupling measurements. Line positions were determined automatically by computer software using the Varian S-124XL Fourier transform accessory. ^{13}C–^1H couplings were eliminated using broadband ^1H noise-modulated decoupling. Complete shift and coupling data will appear in a later publication.[6]

The most striking aspect of the data is the high shielding exhibited by the ylide carbons, comparable with that of the aliphatic analog **11**, a conjugate acid. Compound **10** has a carbon which is definitely of **1b** type and shows the expected deshielding of the olefinic phosphorus-bound carbon. This deshielding is reasonable in light of the analogous methine carbon shift in the enol form of acetylacetone of 99 ppm[7] and the expected ~16 ppm shielding in replacing its $COCH_3$ group with a proton and ~10 ppm shielding in replacing a proton on an sp^2 carbon with a Ph_3P^+ group. Other examples of pure sp^2 carbon bound to phosphorus are those in the triphenylphosphonium group. Their shifts range from 126 to 128 ppm and their directly bonded ^{13}C–^{31}P couplings from 89 to 92 Hz, values far from those of the ylide carbons. *It is clear that* **1b** *does not provide a reasonable bonding description for phosphorus ylides* although it is commonly written as an explanation of the existence of cis–trans isomerism. Structure **1c** places a large negative charge density on the ylide carbon. This is consistent with the high shieldings experienced by the ylide carbon and is reminiscent of the high shieldings observed in alkyl-

---

(1) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966; R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, **92**, 3929 (1970); D. B. Boyd and R. Hoffmann, *ibid.*, **93**, 1064 (1971).

(2) See, for example, R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, London, 1965.

(3) D. M. Crouse, A. T. Wehman, and E. E. Schweizer, *Chem. Commun.*, 866 (1968); H. J. Bestmann and J. P. Snyder, *J. Amer. Chem. Soc.*, **89**, 3936 (1967).

(4) F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841 (1968).

(5) Phosphorus ylides have been examined using ^1H and ^{31}P nmr; (a) ^1H nmr data appear in ref 3 and 4 as well as in H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 604 (1968); W. Malisch, D. Rankin, and H. Schmidbaur, *ibid.*, **104**, 145 (1971); R. K. Harris, J. R. Woplin, K. Issleib, and R. Lindner, *J. Magn. Resonance*, 7, 291 (1972); (b) ^{31}P nmr studies on the series $Ph_3P{=}CR_2$, R = alkyl: S. O. Grim, W. McFarlane and T. J. Marks, *Chem. Commun.*, 1191 (1967); (c) ^{31}P nmr data on air-stable ylides are discussed in A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 76–79.

(6) G. A. Gray, submitted for publication.

(7) J. H. Billman, S. A. Sojka, and P. R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2034 (1972).