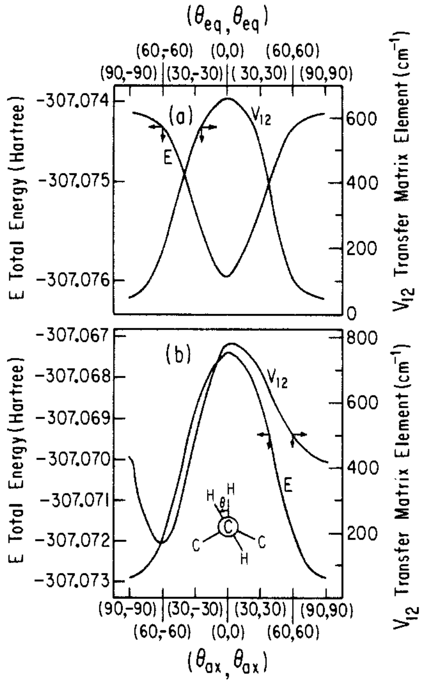

Figure 1. Total energy E (hartree) and transfer matrix element V_{12} (cm^{-1}) along the seam of crossing between diabatic energy surfaces for *t*-(e,e)-**1** (a) and *t*-(a,a)-**1** (b) as a function of dihedral angle θ (deg). The insert defines θ with Newman projections along the methylene–cyclohexane C–C bond.

and 4-biphenylyl groups of the compounds used in the experiments. Therefore, MM2 force field calculations[8] were carried out for the corresponding 1,4-diphenylcyclohexanes **2**. It was found that *t*-(e,e)-**2** does indeed prefer a 0,0-conformation while the minimum for *t*-(a,a)-**2** lies close to 55,55. Comparing the matrix elements of the two conformers of *t*-**1** at rotation angles corresponding to the MM2 energy minima for *t*-**2**, it is predicted that molecules with the *t*-(e,e) geometry will react considerably faster than those with a *t*-(a,a) structure. It is noteworthy that very large rate differences are predicted for the different rotamers without any change in distance.

The lack of symmetry in *c*-(e,a)-**1** required a search on a two-dimensional grid to locate a possible seam. The regions near 60,60 and 60,–60 are close to isoenergetic and give interaction energies of 100 and 170 cm^{-1}, respectively. At no point was $V_{a,b}$ found to exceed one-third of the maximum value found for the trans isomers. the MM-2 minimum energy for *c*-(e,a)-**2** is found for 0-e and 55-a which is not a crossing point in *cis*-**1**. The $V_{a,b}$ at this geometry for *c*-(e,a)-**1** is about 8 times smaller than that of *t*-(e,e)-**1** at its minimum energy. This finding is in qualitative agreement with the experimental data.

To improve the reliability of these predictions the two extreme rotamers of *t*-(e,e)-**1** were calculated with a split-valance 4-31G basis set. Qualitatively, the same results were obtained, with the 0,0-rotamer giving the largest interaction (1790 cm^{-1}) and the lowest energy. To check the magnitude of this element against the experimental rate constant (2 × 10^{9} s^{-1}) one has to consider the reduced electron densities at the attachment positions of 4-biphenylyl and 2-naphthyl negative ions, ρ_b and ρ_n, compared to the essentially unit densities in our model. From densities determined by ESR[9] of the respective negative ions, an interaction energy of 215 cm^{-1} is obtained (1790 $(\rho_b\rho_n)^{1/2}$) fairly close to that estimated from the experimental rate (150 cm^{-1}) using theory essentially due to Jortner.[10]

Finally, to give an estimate of the magnitude of the through-space interaction, calculations with 4-31G and 6-311G** basis sets were carried out on the interaction of a methyl radical with a planar methyl anion at the same distance and geometry as in *t*-(e,e)-**1**, the latter basis set having a better tail behavior essential in the through-space interaction.[11] The calculated through-space interaction, 2.7 and 19.8 cm^{-1}, respectively, is fairly small.

In summary, as far as the aromatic anions in solution are described well within the flexible valence basis set, these calculations together with the experimental results show clearly that intramolecular long-distance ET proceeds mostly by through-bond interaction involving the spacer and does so in a very stereospecific manner. Similar mechanisms may be at work in intermolecular ET where molecules are held apart by rigid matrices[12] or by proteins.[13] In these cases the solvent molecules or the protein fragment will provide the MO's for interaction, although the coupling should be weaker.

Acknowledgment. G.L.C. is grateful to the Japanese Ministry of Education for financing a visiting professorship at IMS during which the work was carried out. The work at IMS was supported in part by a Grant-in-Aid from the Japanese Ministry of Education to one of the authors (K.O.). Ab Initio MO calculations were carried out at the Computer Center of IMS. Work at The University of Chicago was supported by NSF Grant CHE-8218164 and work at Argonne National Laboratory was supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

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(8) The molecular mechanics (MM2) program was written by N. Allinger and Y. H. Yuh, University of Georgia (1980), and was obtained from the Quantum Chemistry Program Exchange, University of Indiana.

(9) Densities used are for an unsubstituted naphthalene negative ion at position **2** (0.072) and a biphenyl negative ion at position **4** (0.202): Atherton, N. M.; Weissman, S. I. *J. Am. Chem. Soc.* **1961**, *83*, 1330. Snyder, L. C.; Amos, T. *J. Chem. Phys.* **1965**, *42*, 3670.

(10) Kestner, N. R.; Jortner, J.; Logan, J. *J. Phys. Chem.* **1974**, *78*, 2148. Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. The relative Franck–Condon factors were calculated from rate data listed in ref 1b, making use of a formalism described in ref 11.

(11) If a diffuse anion function is included in this model calculation, the through-space interaction becomes much larger, e.g., 721 cm^{-1} with 6-311G** + anion sp (α = 0.0438). However, this basis function is not very appropriate for a real system which is composed of delocalized aromatic anions measured in solution.

(12) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.

(13) Nocera, D. G.; Winkler, J. R.; Yocom, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5145. Isied, S. S.; Kuehn, C.; Worosila, G. *J. Am. Chem. Soc.* **1984**, *106*, 1722. McGourty, J. L.; Blough, N. V.; Hoffman, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 4470.

Electron-Transfer Pathways in the Hydride Abstraction by Ph_3C^+ from Exo-Substituted Cyclohexadiene Fe(0) Complexes: A Key Step in the Synthesis of Heterobifunctional Cyclohexadienes from Benzene

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Double nucleophilic attack at a transition-metal benzene complex[1–6] is an attractive way to make heterobifunctional cyclo-

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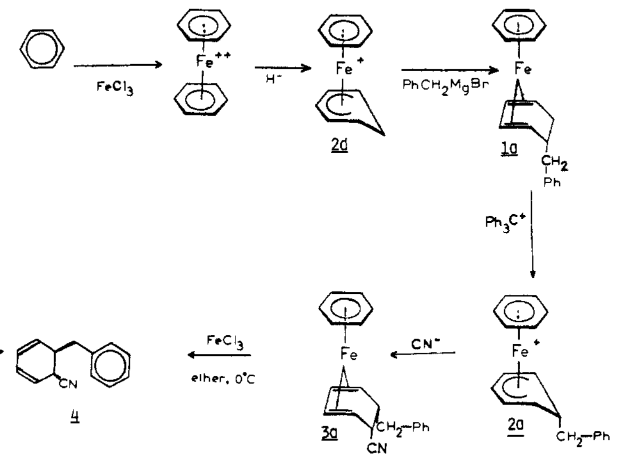
(1) (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (c) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638. (d) Brookhart, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161.

(2) (a) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. Jones, D.; Wilkinson, G. *Ibid.* **1971**, 3807. (b) Grundy, S. L.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 379.

0002-7863/86/1508-1320$01.50/0

hexadienes.[3,4,7] With $Fe(\eta^6\text{-}C_6H_6)_2^{2+}$ reagents, only monosubstituted cyclohexadienes[5,6] are accessible (the first nucleophile can be a hydride,[8] but not a carbanion[9]). We wish to report that (i) a hydride can be easily removed by Ph_3C^+ from exo-substituted cyclohexadiene $Fe^0(C_6H_6)$ complexes by an ET (electron transfer) path and (ii) subsequent attack of a carbanion (KCN) on the cations **2** leads to heterobifunctional cyclohexadienes **4** via the Fe(0) complexes **3** followed by decomplexation effected by $FeCl_3$.



The regio- and stereocontrol is indicated inter alia by the X-ray crystal structure of $Fe(\eta^4\text{-}exo,exo\text{-}5\text{-}(PhCH_2)\text{-}6\text{-}CNC_6H_6)(\eta^6\text{-}C_6H_6)$ (**3a**).

The trityl cation has been extensively used to remove a hydride from organic and organometallic compounds.[10] However, although parent 1,3-cyclohexadiene transition-metal complexes follow this trend,[10d-f] this is not the case for exo-substituted cyclohexadiene complexes for steric reasons[11] (unless they bear a $SiMe_3$ group in 2-position[11c]). Thus, a strategy taking into account this steric inhibition must be delineated. The ET route stands as an alternative if (i) the Fe(0) complexes are electron-rich and ET to Ph_3C^+ is favorable (the relative redox potentials of Ph_3C^+ (0.2 V vs. SCE)[13] and **1** (−0.040 V vs. SCE) favor ET)[12,13c] and (ii) the 17-electron Fe(I) complexes formed are stable enough under the reaction conditions to transfer a H atom to $Ph_3C\cdot$.[12] Addition of 1 mol of $Ph_3C^+PF_6^-$ to a CH_2Cl_2 solution of $Fe(\eta^4\text{-}C_6H_7R)(\eta^6\text{-}C_6H_6)$ [R = CH_2Ph (**1a**), $CH_2C_6Me_5Fe^+Cp$ (**1b**), $CHS(CH_2)_3S$ (**1c**), H (**1d**)][5,6] at −90 °C followed by warming up to 20 °C over 1 h gives the parent complex $[Fe(\eta^5\text{-}C_6H_7)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**2d**) in varying yields, as the only tractable organoiron product. Thus the first functional group is lost in these reactions. If, on the other hand, the reaction medium is allowed to react for 2 h between −50 and −40 °C, excellent yields (90–95%) of the red, air-stable, exo-substituted cyclohexadienyl complexes **2a–c** are obtained after extraction with CH_3CN and crystallization from $CH_3CN\text{-}Et_2O$.[14] The success of these reactions greatly depends on the stability of the intermediate 17-electron Fe(I) cations $\mathbf{1}^+$ which are stable up to −40 °C and can react by H atom transfer to $Ph_3C\cdot$. On the other hand, above −40 °C, $\mathbf{1}^+$ decomposes by loss of $R\cdot$.

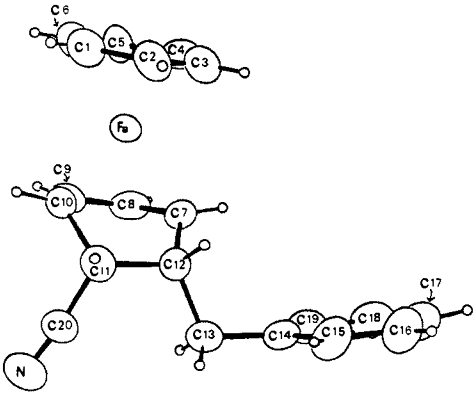


Figure 1. ORTEP view of $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}exo,exo\text{-}5\text{-}(PhCH_2)\text{-}6\text{-}CNC_6H_6)$ (**3a**). For clarity of the perspective view of the molecule, the important thermal agitation of the benzene atoms is lowered to 25% probability. All the remaining atoms have 50% probability. The benzene ring and the H diene carbon are both planar. Folding angle of the cyclohexadiene: 42.2°. Mean Fe–C(diene) distance: 2.024 Å. Mean Fe–C(benzene) distance: 2.020 Å. Fe–benzene(ring centroid): 1.536 Å. The CN group is not quite colinear with C_{11} (173.9°), possibly due to a packing effect.

If the reaction is performed at −40 °C, the EPR spectra of the reaction mixture show the two signals of the 17-electron Fe(I) intermediate $\mathbf{1a}^+$ ($g_\parallel = 2.1983$; $g_\perp = 2.1278$) and that of $Ph_3C\cdot$ ($g = 2.0024$) in a spectrum recorded at −140 °C. The decomposition of the Fe(I) complexes is noted by "irreversible" broadening of its characteristic signals above −40 °C whereas the characteristic signals of $Ph_3C\cdot$ are observed (16 lines at 0 °C, $g = 1.999$, reversibly giving the single line at −130 °C). The steric constraints for H· transfer (between **1** and Ph_3C^+) and H^- transfer (between $\mathbf{1}^+$ and $Ph_3C\cdot$) are similar. However, the extreme reactivity or unstability of the 17-electron species $\mathbf{1}^+$ accounts for a much lower kinetic barrier.

Access to exo-functional cyclohexadienyliron complexes **2a–c** opens the route to exo,exo heterobifunctional cyclohexadiene complexes **3** by orbital-controlled[6] nucleophilic attack of a functional carbanion.[5,6] Thus, reaction of **2a,b** with KCN in acetone at ambient temperature (**2a**, 72 h; **2b**, 12 h) gives the orange, slightly air sensitive complexes **3a,b** (crystallization from ether–pentane: 87% of **3a**, 0.33-mmol scale, 44% yield of **3b**, 0.035-mmol scale). The X-ray crystal structure of **3a**,[15] the first

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(3) Lai, Y. H.; Tam, W.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *216*, 97.

(4) (a) Chung, Y. K.; Choi, H.; Sweigart, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 4225. (b) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem.* **1985**, *107*, 2388.

(5) Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 3381.

(6) Astruc, D.; Michaud, P.; Madonik, A. M.; Saillard, J.-Y.; Hoffmann, R. *Nouv. J. Chim.* **1985**, *9*, 41.

(7) (a) Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 488. (b) Pearson, A. J.; Ong Chi Wi *J. Org. Chem.* **1982**, *47*, 3780.

(8) Nesmeyanov, A. N.; Vol'kenau, N. A., Bolesova, I. N.; Polkovnikova, L. S. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 1130.

(9) Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437.

(10) (a) Green, M. L. H.; Nagy, P. L. *J. Organomet. Chem.* **1963**, *1*, 58. (b) Rosan, A.; Rosenblum, M.; Trancrede, J. *J. Am. Chem. Soc.* **1973**, *95*, 3062. (c) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (d) Fischer, E. O.; Fischer, R. D. *Angew Chem.* **1960**, *72*, 919. (e) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332. (f) Birch, A. J.; Haas, M. A. *J. Chem. Soc. C* **1971**, 2465. (g) Sanders, Cohen, L.; Giering, W. P., Kennedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430. (h) Cohen, L.; Giering, W. P.; Kennedy, D.; Magatti, C. V.; Sander, A. *J. Organomet. Chem.* **1974**, *65*, C57. (i) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291. (j) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299. (k) Birch, A. J.; Jenkins, I. D. In "Transition Metal Organometallics in Organic Synthesis", Alper, H., Ed.; Academic Press: New York, 1976; Chapter 1, p 1. (l) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. (m) Green, M.; Greensfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18.

(11) (a) Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans* **1973**, *1*, 1882. (b) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463; *Transition Met. Chem.* **1981**, *6*, 67. (c) Paquette, L. A.; Daniels, R. G.; Gleiter, R. *Organometallics* **1984**, *3*, 560.

(12) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570.

(13) (a) Volz, H.; Lotsch, W. *Tetrahedron Lett.* **1969**, 2275. (b) Kothe, G.; Söumermann, W.; Baumgärtel, H.; Zimmermann, H. *Ibid.* **1969**, 2185. (c) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, S. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020.

(14) Analytical and NMR (^{13}C and ^1H) data are found in the supplementary material.

(15) Slightly air sensitive crystals suitable for X-ray analysis were obtained by slow crystallization from ether at −20 °C. Crystal data and refinements results: $C_{20}CH_{20}FeN$, monoclinic, $P2_1/c$, $a = 11.933$ (3) Å, $b = 11.925$ (3) Å, $c = 11.185$ (4) Å, $\beta = 93.03$ (4)°, $v = 1589.4$ (6) A^3, $Z = 4$, $\mu = 0.94$ mm^{-1}. The crystal (0.25 × 0.25 × 0.2 mm) was mounted under inert atmosphere in a glass capillary. The data collection on a Enraf-Nonius CAD-4 diffractometer (λ(Mo $K_\alpha = 0.71064$ Å, scan $w/2$, $\theta = 1°$, $\theta_{max} = 25°$) gave 2086 unique data with $I > 2\sigma(I)$. The Fe atom was located with a Patterson map. Remaining atoms were located by Fourier differences. After isotropic and anisotropic refinements, all the hydrogen atoms are located in the same Fourier difference (between 0.61 and 0.27 e A^{-3}). The best refinement (x, y, z, β for non-hydrogen atoms, benzene hydrogen fixed) gives $R = 0.049$ and $R_w = 0.055$.

one of an Fe(0) benzene complex, confirms that both substituents are located in an exo position (Figure 1). New 5,6-*Z* disubstituted cyclohexadienes can be synthesized by decomplexation of Fe(0) complexes such as **3**. The ligands are cleanly disengaged from **3a** by oxidation using $FeCl_3$ in ether at 0 °C. After extraction with CH_2Cl_2, filtration on alumina, and removal of volatiles in vacuo, the ^1H and ^{13}C NMR spectra of the brown oil indicate that **4**[14] is the only organic compound obtained other than benzene (quantitative spectroscopic yield). The mass spectrum at 20 °C shows the molecular peak (m/e^+ calcd 195.1048; found 195.1048) and indicates the absence of aromatization. The latter is significant at 35 °C, as indicated by the peak $(m - 2/e)^+$ and corresponds to the formation of $(o\text{-}C_6H_4)(CH_2Ph)(CN)$.

Finally, we believe the present strategy applies to the transition-metal-mediated heteropolyfunctionalization of various unsaturated hydrocarbons. Many "alkyl abstraction reaction" in electron-rich hydrocarbon transition-metal complexes[16] can now be explained and circumvented as shown here.

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Supplementary Material Available: Thermal parameters, bond angles, and bond lengths for **3a**, analytical and spectroscopic (^1H and ^{13}C NMR) data for **2a–c** and **3a,b**, ^{13}C NMR spectra of **2a–c**, **3a**, and **4**, and EPR spectrum of **1a** + Ph_3C^+ (14 pages). Ordering of information is given on any current masthead page.

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(16) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S.; Petrakova, V. A. *J. Organomet. Chem.* **1975**, *85*, 365. (b) Tetrahedron Report No. 157: Astruc, D. *Tetrahedron* **1983**, *39*, 4095.

Molybdenum Metalloazines. New Reagents for C=C Bond Formation by an Organometallic Analogue of the "Wittig" Reaction

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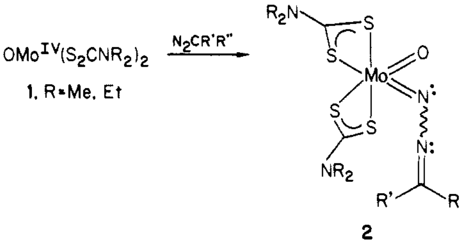
We have long been interested in developing new, practicable organometallic methodology for generalized olefin synthesis. We have noted[1] that $Cp_2Zr(PR_3)_2$ reacts with simple phosphoranes (although slowly and in low yield) to give Cp_2Zr–alkylidenes; a variety of these (best made by an alternate route) condense with carbonyl-group-containing materials to give olefins in high yield.[2] We have also found that simple phosphoranes and $Cp_2Mo(PR_3)$ analogues react readily, but the resulting product condenses rapidly with an additional equivalent of ylide to give only the symmetrical olefin.[3] We have now examined reactions between low-valent molybdenum compounds and diazoalkanes, another class of readily available organic "ylides" which has already enjoyed wide utilization as precursors of reactive carbene complexes through interaction with a variety of metallic complexes.[4] In contrast to our results using phosphoranes[3] or of others with regard to diazo compound activation,[4] we find that diazoalkanes react rapidly and in high yield with simple molybdenum complexes to give adducts, "metalloazines"; these demonstrate susceptibility to nucleophilic attack on the carbon end of the coordinated diazo unit. Conventional phosphoranes react with these adducts (which, ultimately, are carbonyl group derivatives) to give olefins in an organometallic variation on the "Wittig" reaction. In contrast to this classical procedure which gives phosphine oxide in addition to olefin, this new process results in regeneration of the *free* phosphine starting material as well as the starting molybdenum compound.

An easy synthesis of molybdenum "metalloazines" is accomplished by using $OMo^{IV}(S_2CNR_2)_2$ (**1**) (R = Me, Et) which is prepared from readily available $Na_2MoO_4{\cdot}2H_2O$ and NaS_2CNR_2. In a typical procedure, a THF solution of **1** (0.4 g, 0.94 mmol in 15 mL of THF) was treated with a THF solution of 1.5 equiv of phenyldiazomethane[5,6] at room temperature to give an orange-red solution. After removal of the solvent, the residue was dissolved in a minimum of toluene and filtered. Addition of pentane to the filtrate and cooling resulted in the formation of metalloazine **2a** in 95% yield as orange crystals (eq 1). In an analogous manner, metalloazines of Ph_2CN_2 and $PhMeCN_2$ were prepared and isolated.[7] Metalloazines of $CH_3(CH_2)_2CHN_2$, $CH_3CHCH_3CHN_2$, 4-(diazomethyl)cyclohexene, and $(CH_3)_3C$-CHN_2 were prepared and used in subsequent reactions without isolation.[8]



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NMR analysis of metalloazines derived from diethyldithiocarbamate ligands is made difficult by complex, overlapping patterns for the ethyl groups, which suggests a molecule of low symmetry. NMR analysis of $OMo(NNCPh_2)(S_2CNMe_2)_2$ (**2h**) and $OMo(NNCHPh)(S_2CNMe_2)_2$ (**2i**) is more revealing. At room temperature, **2h** exhibits a single, broad methyl peak in the ^1H NMR (CD_2Cl_2 δ 3.30; C_6D_6 δ 2.27) and in the ^{13}C NMR (C_6D_6 39.47 ppm); however, at 213 K ^1H NMR analysis (in $CDCl_3$) reveals three peaks (δ 3.12, 3.28, and 3.40) in the methyl region (relative intensities 1:1:2).[15] Analysis by ^{13}C NMR at 213 K (in $CDCl_3$) showed two peaks at 199.09 and 201.86 ppm assigned to the dithiocarbamate carbons of a "cis"-substituted complex analogous to the starting *cis*-dioxo complex. The ^{13}C methyl region for **2h** appears as four signals at 40.18, 40.63, 41.22, and 41.27 ppm. NMR analysis of $OMo(NNCHPh)(S_2CNMe_2)_2$ (**2i**) suggests the presence of four isomeric structures, ratios for which are solvent-dependent (based on integration of benzylic proton signals at 5.16, 5.79, 6.19, and 6.49 ppm in benzene (relative intensities 40:2:6:1) or at 4.73, 5.29, 5.40, and 5.52 ppm (relative intensites 4:2:1:1) in methylene chloride). The methyl region in either the carbon or proton spectra is complex, and eight major and several minor signals are revealed, consistent with the cis and trans isomers shown, in which rotation about the nitrogen dithiocarbamate bond is slow on the NMR time scale.[16]

The susceptibility to nucleophilic attack at the metalloazine carbon in these complexes is indicated in their reaction with amines or ylides. For example, **2a** reacts with *tert*-butylamine to give Ph(H)C=N(*t*-Bu) (50%). In their reaction with ylides, the molybdenum metalloazines behave as active carbonyl equivalents in a "Wittig-type" reaction. The react rapidly with phosphoranes at room temperature with evolution of dinitrogen and formation of the olefin. Significantly, the starting organometallic complex is regenerated, as is *free* triphenylphosphine (Table I). For example, when a THF solution containing 2 equiv of $Ph_3P{=}CH(CH_2)_3CH_3$ (25 mg, 0.08 mmol, in 2 mL of THF)[17] is added to a THF solution of 1 equiv of **2a** (20 mg, 0.04 mmol in 4 mL of THF), immediate evolution of nitrogen is observed. Analysis by GC indicates olefin is formed in 90% yield (Z/E = 1.25).[18,20,21]

The reactivity of a molybdenum "metalloazine" toward a phosphorane is somewhat less than that of the corresponding carbonyl compound. For example, when 1 equiv of $Ph_3P{=}CH(CH_2)_3CH_3$ was added to a 1:1 mixture of **2a** and *p*-tolualdehyde, less than 5% of the resulting products originated from the metalloazine, indicating an almost exclusive selectivity of the ylide

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(1) Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1.

0002-7863/86/1508-1322$01.50/0