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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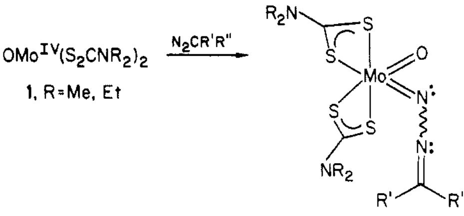
We have long been interested in developing new, practicable organometallic methodology for generalized olefin synthesis. We have noted[1] that $Cp_2Zr(PR_3)_2$ reacts with simple phosphoranes (although slowly and in low yield) to give Cp_2Zr–alkylidenes; a variety of these (best made by an alternate 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 $(CH_3)_3C\text{-}CHN_2$ were prepared and used in subsequent reactions without isolation.[8]



(1)

2

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 $Ph(H)C{=}N(t\text{-}Bu)$ (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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Table I.

$$\underset{\mathbf{2}}{\mathrm{OMo(NNCR'R'')(S_2CNR_2)_2}} + \mathrm{Ph_3P{=}CR_1R_2} \rightarrow \mathrm{R'R''C{=}CR_1R_2} + \mathrm{N_2} + \mathbf{1} + \mathrm{PPh_3}$$

metalloazine				yields^a of R″R′C=CR$_1$R$_2$ (%, Z/E)		
2	R′	R″	R	R$_1$ = R$_2$ = H	R$_1$ = H; R$_2$ = *n*-Bu	R$_1$ = H; R$_2$ = Ph
a	H	Ph	Et	70	90 (1.25)	99 (0.4)
b	Me	Ph	Et	65	10 (0.5)	55 (1.2)
c	H	Pr	Et	40	50^b	70 (0.6)
d	H	*i*-Pr	Et	40	99 (0.3)	80 (0.1)
e	H	*t*-Bu	Et	99	25 (1.5)^c	70 (1.0)^c
f	H	4-cyclohexenyl	Et	35	99 (0.14)	99 (0.1)
g	Ph	Ph	Et	40^d	54	0^c
h	Ph	Ph	Me	70	70	0^c

^{a}All reactions were run at room temperature for 24 h with 2 equiv of ylide unless otherwise stated. THF or toluene were used as solvents. Yields were determined by GC and all products were confirmed by GC/MS analysis. ^{b}Only one isomer observed. ^{c}Reaction was heated at 60 °C. ^{d}See footnote 18.

for reaction with the aldehyde. In contrast, reaction of the ylide with 1:1 mixtures of **2a** and ketone (acetophenone) or **2a** and ester (methyl benzoate) resulted exclusively in products derived from the metalloazine.

The olefin synthesis described above directly parallels conventional "Wittig" chemistry with one important difference: In conventional "Wittig" chemistry, when a carbonyl group is converted to an olefin, the "redox couple" is balanced by conversion of a phosphine to a phosphine oxide. Apart from recovery of triphenylphosphine oxide as a problem of practical consequence, the inability to easily recycle it to triphenylphosphine is a major negative attribute of the "Wittig" sequence. In the "Wittig analogous" reaction described herein, a carbonyl group starting material is sequentially converted to an olefin through its hydrazone and diazoalkane derivatives. Thus, ultimately, *only hydrazine is oxidized to dinitrogen* to balance the reduction of the carbonyl group to the olefin, and both the organometallic and the triphenylphosphine are readily recovered from the reaction, to be recycled.

Acknowledgment. We acknowledge support for this work given by the NSF and NIH.

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(2) Effectively this would provide long-chain analogues of the Tebbe Reagent; see: Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

(3) Smegal, J. A.; Schwartz, J., unpublished results.

(4) For example, see: Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–812 and references cited therein.

(5) Kaufman, G. M.; Smith, J. A.; VanderStouw, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1965**, *87*, 935.

(6) A small excess of phenyldiazomethane was used to ensure complete conversion of $\mathrm{OMo(S_2CNR_2)_2}$ to $\mathrm{OMo(NNCHPh)(S_2CNR_2)_2}$ (which does, however, react slowly with $\mathrm{PhC(H)N_2}$ to give *cis*- and *trans*-stilbene, $\mathrm{N_2}$, and **1**).

(7) For **2g** empirical formula $\mathrm{C_{23}H_{30}N_4OS_4Mo}$: C, H, N, O, S, Mo; $\nu_{\mathrm{Mo{=}O}}$ = 883 (s), 916 (sh) cm^{-1}; for **2a**, $\nu_{\mathrm{Mo{=}O}}$ = 893 (s), 914 (sh) cm^{-1}.

(8) In preliminary studies we found that $\mathrm{Cp_2Mo(PPh)_3}$[9] (**3**) could also be converted to a metalloazine as follows. A toluene solution of **3** (0.2 g, 0.88 mmol in 10 mL of toluene) was cooled to −30 °C and a toluene solution containing 1.5 equiv of phenyldiazomethane[5] (1.32 mmol in 4 mL of toluene) was added to give a yellow-brown solution. Concentration of the reaction mixture, addition of pentane, and cooling resulted in the formation of red-brown solid **4**. The absence of $\mathrm{N_2}$ formation during the reaction of **3** with the diazo compound and the formation of the corresponding hydrazone upon hydrolysis of **4** indicates the presence of the entire diazoalkane unit in **4**, formulated as $\mathrm{Cp_2Mo^{IV}(NNCHPh)}$ (^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.85 (s, Cps 10 H), 6.0 (s, $\mathrm{N_2C}$*H*Ph, 1 H), 7.6, 7.0 (m, Ph, 5 H)). Although a definitive assignment of the bonding mode of the diazo moiety to Mo cannot be determined from the NMR data, the chemical shift of the iminic hydrogen in **4** is consistent with an end-on binding mode by analogy with another Mo$^{\mathrm{IV}}$ complex, $\mathrm{[MoF(NNCHPh)(dppe)_2]BF_4}$ [^{1}H NMR ($\mathrm{CDCl_2}$) δ 5.6 (s, NNC*H*Ph, 1 H)], for which end-on binding of the diazo unit was determined through X-ray crystallographic analysis of a tungsten analogue.[10-13]

(9) Geoffroy, G.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410–2414.

(10) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740–5748.

(11) Chatt, J.; Head, R. A.; Hitchcock, P. B.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1977**, *133*, C1. A structure was determined by X-ray crystallography of a representative example, $\mathrm{[WBr(NNCMe_2)(dppe)_2]Br}$, of a series of compounds of this type including $\mathrm{[MoF(NNCHPh)(dppe)_2]BF_4}$, all of which were synthesized by the same method.

(12) For a unique Mo analogue, see: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratesmann, A. L. *Inorg. Chem.* **1984**, *23*, 2303–2311. (b) Herrmann, W. A. *J. Organomet. Chem.* **1975**, *84*, C25.

(13) The assertion of a high formal oxidation state requires the assignment of the diazo unit as a $\mathrm{(NNCR_2)^{2-}}$ ligand, an assignment that is substantiated by noting M–N and N–N distances in analogous molybdenum and tungsten diazo adduct structures which have been determined crystallographyically.[12,14]

(14) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295–7301.

(15) A series of W and Mo carbonyl complexes of possibly analogous structure, though of different reactivity, has been prepared. Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537.

(16) A dimeric structure containing bridging diazo units for **2** and **4** cannot be ruled out at this time.

(17) An excess of phosphorane was used to ensure complete reaction of the metalloazine. Although $\mathrm{OMo(S_2CNR_2)_2}$ is regenerated in the procedure shown, olefin synthesis by reaction between the diazo compound and the phosphorane cannot be catalyzed by **1** since these reagents react rapidly to yield a mixture of byproducts (but not the desired olefin).

(18) The α-nitrogen of the diazo adduct unit can also show susceptibility to nucleophilic attack as evidenced by the formation of $\mathrm{Ph_2CNNCH(CH_2)_3CH_3}$ in 70% yield by reaction between sterically crowded **2g** and $\mathrm{Ph_3PCH(CH_2)_3CH_3}$. No reaction occurred between **2g** and $\mathrm{Ph_3PCHPh}$. In an attempt to enhance susceptibility of **2g** to nucleophilic attack, an $\mathrm{AlCl_3}$ adduct (presumably by coordination to the oxo group[19]) was formed. This adduct reacted with $\mathrm{Ph_3PCH_2}$ to give 1,1-diphenylethylene in 40% yield.

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(20) All geometric isomers of **2** are, therefore, reactive.

(21) Metalloazine **4** also reacts with ylides to yield olefins, dinitrogen, and $\mathrm{Cp_2Mo(PPh)_3}$. For example, **4** reacts with $\mathrm{CH_2PPh_3}$ to give styrene (60%).

Metal-Mediated Cycloaddition Reactions of 1,1,2,2-Tetrafluoro-1,2-disilacyclobutene with Cyclohexadiene. Correlation between the Stereochemistry of Intermediates and Reaction Pathways

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Photochemical preparation of silyl–transition-metal compounds and the chemistry of Si–M bonds under photochemical conditions have been a subject of recent interest.[1-4] We recently reported the metal-mediated cycloaddition reactions of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene with 1,3-butadiene derivatives.[5] The reactions proceed via a very unusual 1,1-addition pathway which involves either H- or F-migration depending on the nature of the metal used.[5] Since all butadiene derivatives used in the work involved substituents on carbon 2 and/or carbon 3, it is desirable to investigate the steric effect of the substituents on the target carbons, namely, carbon 1 and carbon 4. One of the prominent examples is cyclohexadiene.

Cycloaddition reaction of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene **1** with cyclohexadiene proceeded smoothly at 100 °C and

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