at -20 °C. The cis/trans ratio calculated from integrated ^{1}H NMR spectra was 30/70.

7: IR (cm^{-1}, Nujol) 2025 (s, ν_{CO}), 1985 (m, ν_{CO}), 1930 (m, ν_{CO}). Anal. Calcd for $C_{30}H_{38}F_3MoO_6SPSi$: C, 48.78; H, 5.19. Found: C, 48.49; H, 4.98.

trans-7: ^{1}H NMR (CD_2Cl_2, 27 °C) δ 12.80 (d, $^3J_{PH}$ = 8.2 Hz, 1 H, C*H*OSiMe$_3$), 7.50 (m, 10 H, Ph), 2.01 (d, $^2J_{PH}$ = 8.5 Hz, 3 H, PMe), 1.77 (s, 15 H, C_5Me_5), 0.01 (s, 9 H, SiMe$_3$); ^{13}C NMR (CD_2Cl_2, -60 °C) δ 341.69 (br, *C*HOSiMe$_3$), 238.10 (d, $^2J_{PC}$ = 24.2 Hz, CO), 131.0 (m, Ph), 178.64 (q, $^1J_{CF}$ = 318 Hz, CF$_3$), 109.25 (s, *C*$_5$Me$_5$), 18.0 (d, $^2J_{PC}$ = 32.0 Hz, PMe), 10.87 (s, C$_5$*Me*$_5$), 1.02 (s, Si*Me*$_3$); ^{31}P NMR (CD_2Cl_2, -60 °C) δ 37.09 (s, PPh$_2$Me).

cis-7: ^{1}H NMR (CD_2Cl_2, 27 °C) δ 13.15 (d, $^3J_{PH}$ = 6.0 Hz, 1 H, C*H*OSiMe$_3$), 7.50 (m, 10 H, Ph), 2.01 (d, $^2J_{PH}$ = 8.5 Hz, 3 H, PMe), 1.79 (s, 15 H, C_5Me_5), 0.02 (s, 9 H, SiMe$_3$); ^{13}C NMR (CD_2Cl_2, -60 °C) δ 341.69 (br, *C*HOSiMe$_3$), 248.50 (d, $^2J_{PC}$ = 24.2 Hz, CO), 131.0 (m, Ph), 242.50 (d, $^2J_{PC}$ = 7.0 Hz, CO), 178.64 (q, $^1J_{CF}$ = 318 Hz, CF$_3$), 109.66 (s, *C*$_5$Me$_5$), 19.8 (d, $^2J_{PC}$ = 31.8 Hz, PMe), 10.87 (s, C$_5$*Me*$_5$), 2.16 (s, Si*Me*$_3$); ^{31}P NMR (CD_2Cl_2, -60 °C) δ 54.50 (s, PPh$_2$Me).

Acknowledgment. We are grateful to Prof. M. J. McGlinchey (Hamilton, Canada) and Drs. J.-R. Hamon, V. Guerchais, and S. Sinbhandit (Rennes) for helpful discussions. We acknowledge M. J. Tudoret for skillful experimental assistance. A gift of molybdenum hexacarbonyl was generously provided by BASF (Ludwigshafen, West Germany).

Supplementary Material Available: Complete tables of bond lengths and angles for 11 and tables of positional parameters and general displacement parameter expressions (5 pages); a listing of observed and calculated structure factors (5 pages). Ordering informations is given on any current masthead page.

"Metalloazine" Complexes of Molybdenum and Zirconium

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A series of "metalloazines" of molybdenum and zirconium was prepared. Molybdenum metalloazines are obtained by reaction between diazo compounds and a molybdenum(IV) complex, $OMo(DTC)_2$ (DTC = a dialkyldithiocarbamate), by oxidative addition. These species are electrophilic at the terminal carbon and add nucleophiles, including ylides. Zirconium metalloazines can be prepared by reaction between zirconium(II) phosphine complexes and diazo compounds, but they are better prepared by metathesis between Cp_2ZrCl_2 and hydrazone derivatives. These species behave as nucleophiles at carbon and condense with aldehydes or ketones to yield olefins. Several mechanistic studies were performed concerning olefination using zirconium metalloazines; these suggest that olefins are formed by a process of antiperiplanar approach of the carbonyl containing substrate to the metalloazine, giving preferentially the *Z* olefin isomer. (A similar antiperiplanar approach is suggested for reaction between molybdenum metalloazines and ylides, given that *Z* olefins predominate in this process, too.)

Introduction

Many transition-metal carbene complexes can be used for alkylidene group transfer: "nucleophilic" complexes have been found to alkylidenate carbonyl-containing materials,[1] and "electrophilic" ones can react with certain ylides in complementary synthetic procedures to give olefins.[2] Conceptually, organic carbonyl-containing compounds might serve as the source of reactive alkylidene units in a metal complex. Our intent was to prepare a series of compounds, $M{=}X{=}C(R_1)R_2$, in which the $[{=}X{=}C(R_1)R_2]$ group could be obtained easily from aldehydes or ketones and for which reactivity paralleled that of their carbene complex analogues, $M{=}C(R_1)R_2$ (with facile loss of "X" in a condensation procedure). We have focused our attention on the chemistry of metallic derivatives of hydrazones since these materials are readily accessible and might mimic the reactivity of carbene complexes, with extrusion of N_2. In fact, elimination of N_2 could provide a powerful driving force for reactions using these "metalloazine" derivatives.

Molybdenum "Metalloazines"

Molybdenum metalloazines[3] (1) can be formed by reaction between low-valent molybdenum complexes and diazoalkanes which are obtained by partial oxidation of hydrazones. In forming the metalloazine the molybdenum center undergoes a formal oxidative addition of the diazo unit.

A general synthesis of molybdenum "metalloazines" was accomplished by using $OMo^{IV}(S_2CNR_2)_2$ which can be obtained[4] from $Na_2MoO_4{\cdot}H_2O$ and NaS_2CNR_2 followed by reduction with triphenylphosphine. The absence of N_2 evolution during the reaction between $OMo(S_2CNR_2)_2$ and diazoalkanes[5] and the formation of the expected hydrazone upon hydrolysis suggest the presence of the entire diazoalkane unit in 1, which we formulate as $OMo(S_2CNR_2)_2(NNCR'R'')$. Transition-metal complex adducts of diazoalkanes are well established,[6] and a variety of

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[1] For example, 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. Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979. Clift, S. M.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 8300. Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953. Aguero, A.; Kress, J.; Osborn, J. A. *J Am. Chem. Soc.* **1986**, *108*, 531. Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399.

[2] For example, see: Fischer, E. O. *Angew. Chem., Int Ed. Engl.* **1964**, *3*, 580. Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 6543. Casey, C. P.; Bertz, S. H.; Burkhardt, T. J. *Tetrahedron Lett.* **1973**, 1421.

[3] Smegal, J. A.; Meier, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1986**, *108*, 1322.

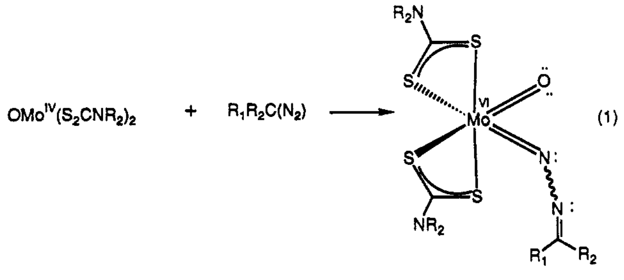
[4] Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612. Barral, R.; Bocard, C.; Sérée de Roch, I.; Sajus, L. *Tetrahedron Lett.* **1972**, 1693.

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

0276-7333/89/2308-2717$01.50/0

Figure 1.

bonding patterns have been elucidated for 1:1 adducts, including several with molybdenum.[7] Of the several structural models suggested for "1:1 adducts", the "end-on" binding mode for 1 seems most likely on the basis of ^{1}H NMR spectral comparison with a known "end-on" bound diazoalkane complex, [MoF(NNCHPh)(DPPE)$_2$]BF$_4$.[8] The assertion of a high formal oxidation state for the metal requires assignment of the diazo unit as a (NNCR$_1$R$_2$)$^{2-}$ ligand, an assignment substantiated by noting M–N and N–N distances in analogous molybdenum and tungsten diazo adduct structures which have been determined crystallographically.[7,9] (A dimeric structure containing bridging diazo units for 1 cannot be ruled out on the basis of these spectral comparisons.) NMR analysis of several of these metalloazines suggested that they adopt a *cis*-dithiocarbamate structure in which the metalloazine unit is end-bonded. For compound **1a**, NMR analysis shows that at least four isomeric compounds are present which likely differ in the stereochemistry of substitution about the nitrogens and the terminal carbon; detailed spectral analysis for these species is complicated by the presence of overlapping spectral peaks.



1

a: R_1 = H; R_2 = Ph; R = Et

b: R_1 = Me; R_2 = Ph; R = Et

c: R_1 = Ph; R_2 = Ph; R = Et

d: R_1 = Ph; R_2 = Ph; R = Me

Molybdenum metalloazines are formal hydrazone adducts and show susceptibility to attack by nucleophiles at the hydrazone-derived carbon, an effect interpreted with reference to the resonance structure shown in Figure 1. In these molybdenum metalloazines, therefore, the electrophilicity of the carbonyl compound from which they are derived is maintained. In fact, molybdenum metalloazines behave as deoxygenated, N$_2$ analogues of ketones or aldehydes in "Wittig"-type reactions: They react rapidly with phosphoranes (at room temperature) with evolution of dinitrogen and formation of the olefin.[10] Molybdenum metalloazines are intermediate in reactivity between simple aldehydes and ketones. For example, when 1 equiv of Ph$_3$P=CH(CH$_2$)$_3$CH$_3$ was added to a 1:1 mixture of 1 and *p*-tolualdehyde, less than 5% of the resulting products originated from the metalloazine; the rest were typical Wittig products of *p*-tolualdehyde. However, reaction of the same ylide with a 1:1 mixture of **1a** and a standard ketone, acetophenone, gave products derived exclusively from the metalloazine. We note phosphorane-based olefin synthesis with metalloazines somewhat favors the *Z* isomer. In fact, *Z*:*E* ratios obtained by conventional Wittig reactions closely parallel those found for metalloazines. The preference for *Z* olefin formation in the Wittig reaction has been interpreted in a variety of ways, one of which involves an antiperiplanar approach of the ylide and the carbonyl group in the key carbon–carbon bond-forming step followed by phosphorous–oxygen bond formation.[11] Since olefin synthesis using metalloazines gives *free* triphenylphosphine, there is apparently no need at *any* stage of the reaction for bonding between P and Mo, and it is therefore possible that an antiperiplanar approach of the ylide to the metalloazine occurs. An important difference exists in a practical sense between these olefin synthesis and conventional Wittig ones. In the classical reaction, conversion of a carbonyl group to an olefin (a formal "redox" process) is accompanied by ultimate oxidation of a phosphine to a phosphine oxide. Using metalloazines both the starting phosphine and the molybdenum complexes are easily recovered in their original, *reduced* forms. Thus to accomplish the "redox couple" of carbonyl-to-olefin, only hydrazine is oxidized to dinitrogen (via the intermediate diazo compound and the metalloazine).

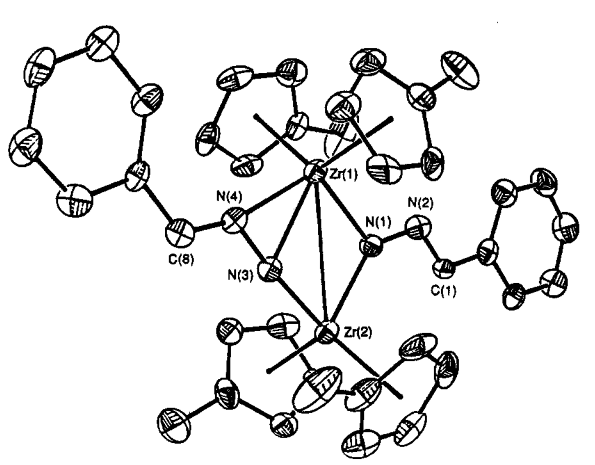


Figure 2. An ORTEP diagram of 4.

$$\mathrm{OMo(NNCR_1R_2)(S_2CNR_2)_2} \quad + \quad \mathrm{Ph_3P{=}CR_3R_4} \longrightarrow$$
$$\mathrm{R_1R_2C{=}CR_3R_4} \quad + \quad \mathrm{N_2} \quad + \quad \mathrm{PPh_3} \quad + \quad \mathrm{OMo(S_2CNR_2)_2} \qquad (2)$$

Zirconium "Metalloazines"

Low-valent zirconium compounds condense with diazoalkanes, as do their molybdenum analogues, to yield zirconium metalloazines (2).[12] These compounds are more

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[6] (a) For example, see: Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800 and references cited therein. (b) Menu, M. J.; Crocco, G.; Dartiguenave, M.; Dartiguenave, Y.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1988**, 1598.

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

[8] Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchica, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740. 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, [WBr(NNCMe$_2$)(dppe)$_2$]Br, of a series of compounds of this type including [MoF(NNCHPh)(dppe)$_2$]BF$_4$, all of which were synthesized by the same method.

[9] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.*, **1983**, *105*, 7295.

[10] The α-nitrogen of the diazo adduct unit can also show susceptibility to nucleophilic attack as evidenced by the formation of Ph$_2$CNNCH(CH$_2$)$_3$CH$_3$ in 70% yield by reaction between sterically crowded OMo(NNCPh$_2$)(S$_2$CNEt$_2$)$_2$ and Ph$_3$PCH(CH$_2$)$_3$CH$_3$. No reaction occurred between this complex and Ph$_3$PCHPh.

[11] A similar argument has been set forth to explain preferences for the *Z* olefin in Wittig reactions in which the *erythro*-betaine is formed on condensation of an ylide with a carbonyl compound and in which collapse of the betaine to olefin is fast. See: House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin, Inc.: Menlo Park, CA, 1972; pp 707–709.

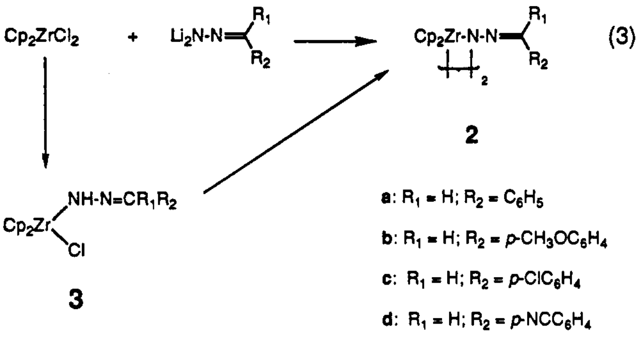
Table I. X-ray Diffraction Data for Complex 4

formula	$C_{38}H_{40}N_4Zr_2 \cdot {}^1/_2C_6H_{14}$
fw	778.4
space group	$P2_12_12_1$
a, Å	19.441 (7)
b, Å	21.922 (9)
c, Å	21.922 (9)
Z	4
d, g/cm³	1.47
cryst dimens, mm	0.16 × 0.20 × 0.24
temp, °C	−100
radiatn	Mo Kα
μ, cm^{-1}	6.2
2θ limits, deg	50
total no. of unique observns	3513
data, $F_o > 3.0\sigma(F_o)$	2996
final no. of variables	409
R	0.056
R_w	0.057

Table II. Selected Bond Distances and Bond Angles for 4

Bond Distances (Å)			
Zr(1)–N(1)	2.180 (7)	N(1)–N(2)	1.36 (1)
Zr(1)–N(3)	2.213 (7)	N(2)–C(1)	1.29 (1)
Zr(2)–N(1)	2.063 (7)	N(3)–N(4)	1.32 (1)
Zr(2)–N(3)	2.004 (7)	N(4)–C(8)	1.29 (1)
Bond Angles (deg)			
Zr(1)–N(1)–N(2)	120.7 (5)	Zr(2)–N(3)–Zr(1)	100.6 (3)
Zr(2)–N(1)–N(2)	139.4 (6)	N(1)–N(2)–C(1)	119.7 (7)
Zr(1)–N(3)–N(4)	73.5 (4)	N(3)–N(4)–C(8)	123.4 (7)
Zr(2)–N(3)–N(4)	174.1 (6)	N(2)–C(1)–C(2)	122.3 (8)
N(3)–Zr(1)–N(1)	76.1 (3)	N(4)–C(8)–C(9)	124.1 (8)
N(3)–Zr(2)–N(1)	83.4 (3)	N(3)–Zr(1)–CX(1)	114.6 (3)
Zr(2)–N(1)–Zr(1)	99.9 (3)	N(1)–Zr(1)–CX(1)	106.4 (3)

easily formed by ligand metathesis between Cp_2ZrCl_2 and $Li_2NNC(H)(R)$, prepared from the hydrazone and 2 equiv of butyllithium in THF at −78 °C. Best yields of these metalloazines result from stepwise syntheses in which the intermediate $Cp_2Zr(Cl)NHNC(H)R$ (**3**) is prepared and isolated.



An ORTEP diagram for methylcyclopentadienyl derivative **4** highlighting the Zr_2N_2 central ring is shown in Figure 2. Crystals of orange-red complex **4** are orthorhombic of space group $P2_12_12_1$. The unit cell (dimensions a = 8.262 (3) Å, β = 19.441 (7) Å, c = 21.922 (9) Å) contains four molecules of **4** and two hexane molecules of solvation which are disordered about the 2-fold screw axis in the X direction (figure available as supplementary material). Table I lists X-ray diffraction data, and selected bond distances and angles are given in Table II (other data are available as supplementary material).

An interesting feature revealed by crystallographic analysis is the unusual, unsymmetrical bridging ligand system which incorporates both the η^1-diazo-bridged form A and the η^2-diazo-bridged form B. The Zr–N bond lengths in $[(\mu\text{-N-}t\text{-Bu})Zr(Me_2)_2]_2$, for example, were found to be 2.071 (1) and 2.060 (1) Å, essentially the same lengths as those in zirconium amido complexes.[13] However, in **4** there was a slight increase in Zr(1)–N(1) and Zr(1)–N(3) bond lengths (2.180 (7) and 2.213 (7) Å, respectively), versus those to Zr(2) (2.063 (7) and 2.004 (7) Å). Clearly one of the bridging N–N ligands is η^2-bonded to Zr(1); Zr(1)–N(4) [2.232 (7) Å] is only slightly longer than is Zr(1)–N(3). In contrast, the other diazo ligand bridges the two zirconium atoms via the terminal N atom. While both symmetrically bridged and η^2-N,N-bonded units are known individually,[14a] these metalloazines and a Ti analogue[14b] are the only ones known in which both types of structural features are present in the same molecule.

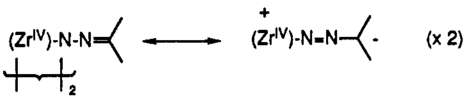


Figure 3.

The ring formed by the terminal nitrogen atoms of the diazo ligands and the two zirconium atoms is planar. The second nitrogen of the symmetrically bridged ligand, N(2), deviates from the plane by 0.16 Å while N(4), which is bonded to Zr(1), is essentially in the plane. Each of the phenyl rings is twisted out of the plant at an angle of 46.4° between them. In the μ-η^1-coordinated ligand, the bonds to the central nitrogen are nonlinear (the angle N(1)–N(2)–C(1) is 119.7 (7)°), and the C(1)–N(2) bond distance of 1.29 (1) Å is consistent with a double bond. The N(1)–N(2) bond distance of 1.36 (1) Å suggests a bond order slightly greater than 1. Similarly, the other diazo ligand has a C(8)–N(4) bond distance of 1.29 (1) Å (for a carbon–nitrogen double bond) and a slightly shorter N–N bond distance (N(3)–N(4) is 1.32 (1) Å). The nitrogen–nitrogen bond distances in both diazo ligands of **4** are shorter than the distance found for the N–N bond in benzylazine.[15] The μ-η^2-coordination of the two nitrogen atoms leads to a nearly linear arrangement for Zr(2) and N(3) and N(4) with a bond angle of 174.1 (6)°. Other structural features for **4** are unexceptional.

The unsymmetrical structure by X-ray analysis for **2a** indicates that it contains two nonequivalent types of cyclopentadienyl ligands and two nonequivalent types of diazo ligands. Examination of the NMR spectrum of **2a** at various temperatures shows it to be a fluxional molecule. The ^{13}C NMR of **2a** (in CD_2Cl_2) shows a single sharp resonance at δ 109.5 (Cp, Cp′) at room temperature. Upon cooling the solution to −80 °C, two broadened resonances are observed at δ 109.7 and 108.2, and warming the solution back to room temperature causes coalescence of the two Cp peaks. No change is observed for the aromatic and iminic carbon in these two NMR experiments, and the proton spectrum of **2a** is not affected by cooling to −80 °C.

Reactions of Zirconium Metalloazines. Zirconium metalloazines are susceptible to electrophilic attack at Zr–N and also at carbon, demonstrating an "umpolung" of reactivity[16] with regard to the hydrazones from which they are derived. Because of low electronegativity of zirconium (many formally zirconium(IV) alkyls undergo facile electrophilic attack), a resonance contribution with negative charge build-up on the metalloazine carbon might be significant.

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(12) Arvanitis, G.; Schwartz, J.; Van Engen, D. *Organometallics* **1986**, *5*, 2157.

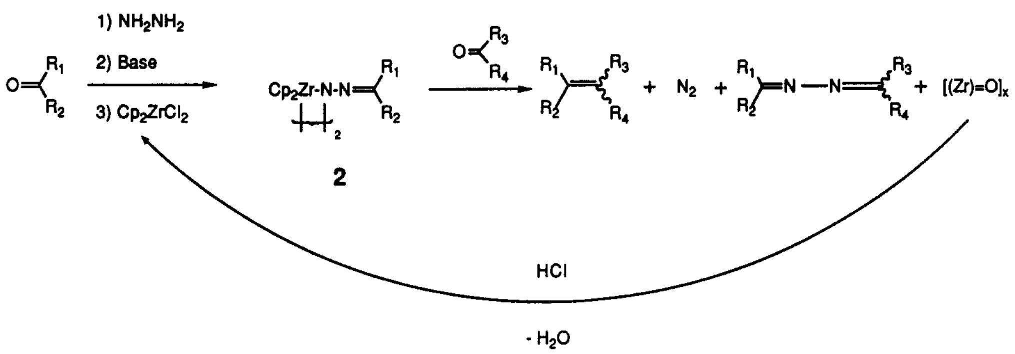
(13) Nugent, W. A.; Harlow, R. L.; *Inorg. Chem.* **1979**, *18*, 2030.

(14) (a) For example, see: Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283. (b) Hughes, D. L.; Latham, I. A.; Leigh, G. S. *J. Chem. Soc., Dalton Trans.* **1986**, 393.

(15) Burke-Laing, M.; Laing, M. *Acta Crystallogr.* **1976**, *B32*, 3216.

(16) Seebach, D.; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

Scheme I



2

The "umpolung" phenomenon is especially interesting with regard to the reaction between zirconium metalloazines and aldehydes and ketones. This procedure, which yields an olefin,[12] formally constitutes the unsummetrical coupling of two carbonyl groups. Unsaturated aldehydes or ketones gave highest selectivities for olefin versus azine formation. The only byproduces of olefin formnation are dinitrogen and a crystalline zirconium (oxo) polymer that can be removed easily from the reaction mixture and recycled to Cp_2ZrCl_2 with anhydrous HCl. Thus in this process, too, the "reduction" of the two carbonyl units to olefin is balanced, ultimately, by the oxidation of N_2H_4 to N_2 and H_2O.

a. Substituent Effects. Metalloazine **2a** was reacted with a series of para-X-substituted benzaldehyde derivatives (**5a**, X = H; **5b**, X = OCH_3; **5c**, X = Cl; and **5d**, X = CN).[17] Since each zirconium metalloazine contains 2 equiv of reactive groups which are likely transferred sequentially to each of 2 equiv of the substrate, rate data for these reactions were measured only for initial phases of each reaction sequence. In this way, a linear Hammett correlation[18] was obtained for olefin formation which showed that electron-withdrawing groups in the aldehyde increased second-order rate constants for this process. Interestingly the rate of azine formation appeared to *increase* with electron-donating ability of the benzaldehyde substituent, suggesting that a strong interaction between the carbonyl group oxygen of the substrate and the zirconium center is important in the transition state leading to formation of azine (but not necessarily to olefin). In a complementary study a series of substituted metalloazine derivatives (**2a**, X = H; **2b**, X = OCH_3; **2c**, X = Cl; and **2d**, X = CN) was reacted with cyclohexanecarboxaldehyde. Reaction rate constants were determined during initial stages of these reactions, too. A linear Hammett correlation was obtained for olefin formation which showed that electron-donating groups on the metalloazine substituent enhanced rates for this process. In this experiment no obvious trend related substituent effects to rates for formation of the azine. The effect of unsaturation in the carbonyl substrate was briefly examined, and it was found that relative rates for olefin formation did not parallel reduction potentials for a pair of carbonyl compounds. For example benzaldenyde and the less easily reduced cyclohexanecarboxaldehyde ($E_{1/2}$ = −1.15 V versus −1.85 V versus SCE for the analogue pentanal[19]) reacted with metalloazine **2a** at comparable rates. Therefore, a mechanism involving electron transfer from the complex to the aldehyde or ketone seems unlikely as the rate-determining step for olefin synthesis.

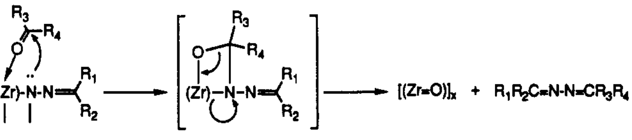


Figure 4.

b. Steric Effects. A series of substituted cyclohexanones was reacted with **2a**. Reactions were run for fixed time, temperature, and concentration conditions so that relative yields of olefin to azine reflect relative rates for reactions leading to these species. Substitution at the 2-position gave approximately equimolar amounts of the olefin and azine, but azine formation occurred more slowly than when cyclohexanone was used; as the site of substitution moved to the 3- and then the 4-positions, the ratio of olefin to azine *dropped*. Thus, substitution *remote* from the carbonyl had a profound effect on the rate of olefin synthesis but not on that of the azine formation. A notable exception was the case in which methoxy substitution existed at the 2-position; here olefin formation was favored over that of azine. In general preference was noted for the *Z* isomer of an olefin, especially for condensation with primary and secondary aldehydes; the *E* isomer was preferred for condensation with 2,2-dimethylpropanal.

c. Proposed Mechanism for Azine Formation. In the reaction between **2a** and para-substituted benzaldehydes, rate constants for azine formation were found to increase with the electron-donating abilities of the benzaldehyde substituent. This likely increases the donor ability of the carbonyl group oxygen to the zirconium center and suggests that a strong interaction between the carbonyl group oxygen and a zirconium center is important in the transition state leading to the formation of azine, consistent with the observation that steric substitution at the 2-position for cyclohexanone *decreased* the rate of azine formation. (The stereochemistry of this process could not be probed.) Azine formation, therefore, appears to resemble Grignard reagent condensations with ketones.[20]

d. Proposed Mechanism for Olefin Formation. We believe that olefin formation occurs by a process of electrophilic attack by the carbonyl group carbon upon the metalloazine carbon center of the organometallic in a process in which C–C bond formation is rate-determining. Electronic substituent effects suggest that carbonyl group coordination to the zirconium is not required in the transition state for C–C bond formation. Steric effects for positional substitution of the carbonyl compounds are different for olefin or azine formation: alkyl substitution at the 2-position of a cyclohexanone had little effect on olefin formation (interpreted that the carbonyl group is *not* coordinated to zirconium at this stage of the olefination

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[18] Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 191.

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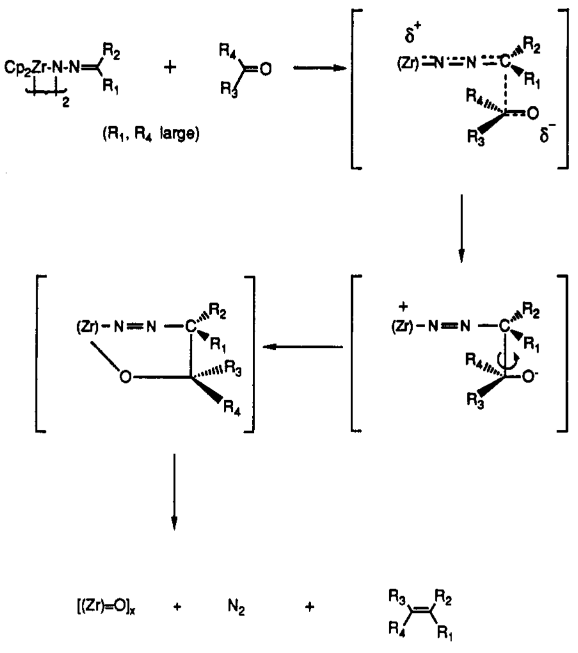


Figure 5.

sequence). Conversely, substitution of the 4-position of the cyclohexanone should have little effect on azine formation since that locus is remove from the site of nitrogen atom attack. However, substitution at this 4-position would engender unfavorable steric interactions with the ligands on the zirconium center in a transition state in which the carbonyl group and the zirconium atom adopt an antiperiplanar arrangement with minimized steric interactions toward C–C bond formation.[11] Rotation about this C–C bond, coordination of the alkoxide oxygen to zirconium, and elimination of N_2 and the [Zr–O] unit yield the preferred *Z* olefin. (Stabilizing a *non-carbonyl* oxygen atom approach to the zirconium should favor olefin formation, as was found for 2-methoxycyclohexanone.)

Conclusions

Molybdenum or zirconium metallozines can be obtained from readily available organic starting materials and simple organometallic precursors. By reaction of either a diazoalkane or a hydrazone derivative with a metal complex in an appropriate oxidation state, azine derivatives of these metals were prepared. Electronegativity differences between the metals and carbon may be responsible for the observed "electrophilic" behavior of molybdenum derivatives and the "nucleophilic" properties of zirconium ones. Thus, interesting possibilities for using transition-metal derivatives of simple organic substrates as synthetic reagents are highlighted by comparing metalloazine complexes of molybdenum and zirconium: common materials, here hydrazones, can show "opposite" reactivity at the carbonyl-derived carbon center by adduct formation with a relatively electronegative metal complex center OMo^{VI}) or with a relatively electrophositive one (Cp_2Zr^{IV}). Metalloazines of both zirconium and molybdenum may be of use as reagents for olefin synthesis since either species reacts with conventional reagents to give them; the byproducts of olefin synthesis are N_2 and H_2O.

Experimental Section

General Information. Reactions using organometallic complexes were conducted under an atmosphere of nitrogen or argon purified by passage through a column of BTS catalyst in reduced form (achieved by heating under a CO stream) to remove oxygen followed by a column of Matheson size 4-Å molecular sieves to remove water. Experiments were performed in a Vacuum Atmospheres drybox or in standard Schlenck equipment under inert atmosphere. Liquid transfers were performed by syringe, and solid transfers were performed under a stream of nitrogen or in the drybox. Organic precursors were prepared in air unless otherwise stated. Tetrahydrofuran, ether, and hydrocarbon solvents were distilled under nitrogen from sodium benzophenone ketyl. Tetraglyme (approximately 5%) was added to hydrocarbon solvents to ensure solubility of the ketyl. All other solvents were distilled under nitrogen from the appropriate drying agent (lithium aluminum hydride, calcium hydride, phosphorus pentoxide, or barium oxide).

Sodium molybdate dihydrate (Aldrich), bis(cyclopentadienyl)zirconium(IV) dichloride (Cp_2ZrCl_2, Boulder Scientific), and other inorganic compounds, including sodium diethyldithiocarbamate trihydrate and sodium dimethyldithiocarbamate dihydrate (Aldrich), were used as received unless otherwise noted. Aldehydes and ketones were distilled from CaH_2 prior to use. Other organic compounds were used as received unless otherwise noted.

Proton nuclear magnetic resonance (NMR) spectra were recorded on either a IBM NR80 (80 MHz), JEOL FX90-Q (90 MHz), Brucker WM250 (250 MHz), or GE QE300 (300 MHz) spectrometer. Chemical shifts are reported in units of δ using either C_6D_5H or TMS as reference in the order: chemical shift, multiplicity, and intensity. ^{13}C NMR spectra were obtained with a JEOL FX90-Q or Brucker WM250 spectrometer. Low-temperature NMR experiments were carried out on a Brucker WM250 spectrometer. Five millimeter screw-cap NMR tubes were fitted with Teflon septa through which reagents were added by syringe.

Analytical vapor phase chromatography was performed on a Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector. Preparative gas chromatography was accomplished on the same instrument fitted with a sample splitter. Yields were obtained by comparison with samples of known concentration. GC–MS analysis was performed on a Hewlett-Packard 5992 GC–MS system with a 9825A computer. High-resolution mass spectra were recorded on an EEI-MS instrument.

Preparation of $MoO(S_2CNEt_2)_2$. The title compound was prepared following a literature procedure[4] except that triphenylphosphine was used in place of ethyldiphenylphosphine. Triphenylphosphine (6.2 g, 23.6 mmol) was added to a solution of 5.0 g (11.8 mmol) of $MoO_2(S_2CNEt_2)_2$ in 90 mL of THF. The reaction mixture was heated to reflux under N_2 for 1.5 h; the red reaction mixture was then filtered, and the filtrate was worked up according to the literature procedure.

Preparation of $OMo(NNCPh_2)(S_2CNEt_2)_2$ (1c). Diphenyldiazomethane (0.2 g, 1.0 mmol) was weighed into a Schlenk flask under N_2, and enough THF was added to dissolve the diazo compound. The molybdenum complex $OMo(S_2CNEt_2)_2$ (0.2 g, 0.49 mmol) was weighed into another Schlenk flask, and enough THF was added to dissolve the complex. The solution containing the molybdenum complex was cooled to −30 °C, and the solution of the diazo compound was slowly added to it via cannula; the reaction mixture changed from red to orange-red in color. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h after which time the THF was removed in vacuo. Crystallization of the product from a toluene/pentane mixture gave the metalloazine (70%) which could be recrystallized from toluene/ether. The burgundy colored crystals thus obtained were dried in vacuo. Recrystallization is not necessary for metalloazines to be used in the olefin synthesis reactions described below. ^1H NMR (room temperature, $CDCl_3$): δ 1.16–1.40 (overlapping triplets, (12), $J \sim 7$ Hz); δ 3.63–3.96 (overlapping quartets, (8), $J \sim 7$ Hz); δ 7.26–7.38, 7.55–7.62 (multiplets, (10)). ^{13}C NMR (208 K, $CDCl_3$); δ 11.97, 12.22, 12.58, 12.71 (four methyl carbons); δ 45.44, 45.85, 46.03 (three methylene carbons; the fourth is seen as a shoulder on the upfield side of the δ 45.85 peak); δ 128.13, 128.77, 128.98, 135.23, 140.19 ($NN{=}CPh_2$); 200.24, 197.84 ($-SC{=}S$ carbons). Anal. Calcd for $C_{23}H_{30}MoN_4OS_4$: C, H, Mo, N, S. IR (KBr pellet): $\nu_{Mo=O}$ = 883 (s), 916 (sh) cm^{-1}.

Other molybdenum metalloazines were made in an analogous manner.

$OMo(NNCHPh)(S_2CNEt_2)_2$ (1a). ^1H NMR (C_6D_6): δ 0.45–0.95 (mult, (12), methyls); δ 2.72–3.32 (mult, (8), methylenes); δ 5.74, 5.84, 6.29 (three singlets, (1) C*H*Ph, relative intensities

2:1:1); δ 7.31–7.93 (mult, (5), Ph). Anal. Calcd for $C_{17}H_{28}MoN_4OS_4$: C, H, N, S.

$OMo(NNCMePh)(S_2CNEt_2)_2$ (1b). ^1H NMR (C_6D_6): δ 0.70 (triplet, (12), *J* = 7 Hz, dithiocarbamate methyls); δ 2.11 (singlet, (3), diazo methyl); δ 3.16 (quartet, (8), *J* = 7 Hz, methylenes); δ 6.98–7.05, 7.53–7.64 (mult, (5), Ph). Anal. Calcd for $C_{18}H_{28}MoN_4OS_4$: C, H, N, S.

$OMo(NNCPh_2)(S_2CNMe_2)_2$ (1d). ^1H NMR (213 K, $CDCl_3$): δ 3.12, 3.28, 3.40 (singlet methyl peaks, (12), relative intensities 1:1:2); δ 7.34–7.39, 7.56–7.60 (phenyl, (10)). ^{13}C NMR (213 K, $CDCl_3$): δ 40.18, 40.63, 41.22, 41.27 (four methyl signals); δ 128.15, 128.54, 128.95, 135.18 (phenyl carbons); δ 140.96 (N_2CPh_2); δ 199.09, 201.86 (dithiocarbamate carbons). Anal. Calcd for $C_{19}H_{22}MoN_4OS_4$: C, H, Mo, N, S.

Reactions between Molybdenum Metalloazines and Phosphoranes. A representative example for olefin synthesis using a molybdenum metalloazine and a phosphorane was performed by addition of $OMo(NNCPh_2)(S_2CNMe_2)_2$ (0.10 g, 0.18 mmol) to a THF solution (10 mL) of triphenylphosphorane (0.099 g, 0.36 mmol) under inert atmosphere at room temperature. Evolution of nitrogen ensued, and aliquots were analyzed by gas chromatography. The reaction mixture was hydrolyzed with water and filtered through a Florosil plug to give a clear colorless filtrate from which the olefin (70%) and triphenylphosphine were recovered. The $OMo(S_2CNMe_2)_2$ was recovered from the Florosil by extraction. The high yield of olefins obtained from a mixture of isomers of 1 suggests that all such isomers are comparably reactive.[3]

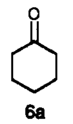
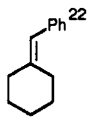
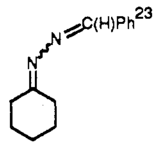
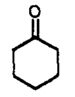
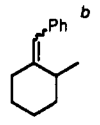
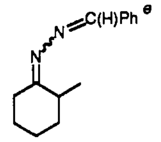
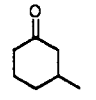
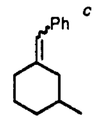
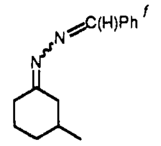
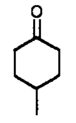
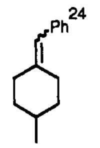
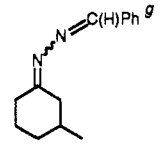
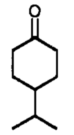
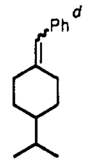
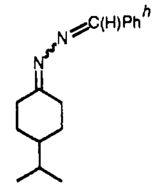
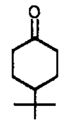
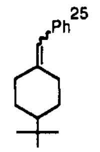
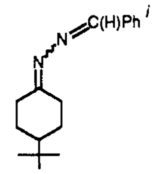
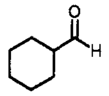
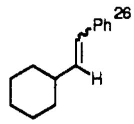
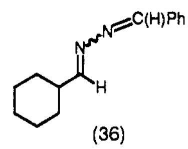
Preparation of $[Cp_2ZrNNCHPh]_2$ (2a) by Reaction of Cp_2ZrCl_2 with $Li_2NNCHPh$. To a solution of phenylhydrazone[21] (0.24 g, 2.0 mmol) in 10 mL of tetrahydrofuran at −78 °C under argon was added *n*-butyllithium (2.6 M, 1.70 mL, 4.4 mmol). The resulting orange solution was transferred via annula to a suspension of Cp_2ZrCl_2 (0.58 g, 2.0 mmol) in 5 mL of THF at −78 °C. The reaction mixture was allowed to reach room temperature, after which time the solvent was removed at reduced pressure. One equivalent of 1,4-dioxane was added to the residue to precipitate LiCl; the residue was then extracted with toluene and filtered. Crystallization at −40 °C resulted in 0.34 g (40%) of the title compound. ^1H NMR (CD_2Cl_2): δ 7.75 (d, *J* = 7.8 Hz, 2 H), 7.70 (s, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 7.29 (t, *J* = 7.7 Hz, 1 H), 5.95 (s, 10 H). ^{13}C NMR (CD_2Cl_2): δ 137.3, 133.5, 129.0, 126.8, 125.3, 109.5. Anal. Calcd for $C_{17}H_{16}N_2Zr$: C, H, N, Zr.

Preparation of $Cp_2Zr(Cl)NHNCHPh$ (3a) from Cp_2ZrCl_2. To a solution of phenylhydrazone (2.40 g, 20.0 mmol) in 25 mL of dry THF at −78 °C under argon was added dropwise *n*-butyllithium (2.5 M, 8.0 mL, 20.0 mmol). The resulting pale yellow solution was added dropwise via cannula to a suspension of Cp_2ZrCl_2 (5.84 g, 20.0 mmol) in 40 mL of toluene at −78 °C. The reaction mixture was stirred as it warmed to room temperature over 8 h. One equivalent of dioxane was added to the mixture, which was then filtered through Celite under inert atmosphere. The solvent was removed under vacuum, and the product was recrystallized (75% yield) from a toluene/hexane mixture at −40 °C. ^1H NMR ($CDCl_3$): δ 7.53 (d, *J* = 7.5 Hz, 2 H), 7.47 (s, 1 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 6.89 (s, 1 H), 5.95 (s, 10 H). ^{13}C NMR (CD_2Cl_2): δ 135.6, 134.1, 129.1, 127.9, 125.6, 113.1.

Reaction of $Cp_2Zr(Cl)NHNCHPh$ (3a) with LDA: An Alternative Preparation of $[Cp_2ZrNNCHPh]_2$ (2a). To a suspension of 3a (1.13 g, 3 mmol) in 10 mL of toluene at −20 °C was added dropwise a solution of lithium diisopropylamide (0.32 g, 3 mmol) in 5 mL of tetrahydrofuran. The reaction mixture was warmed to room temperature, and the solvent was removed at reduced pressure. The residue was extracted with toluene and filtered. Crystallization at −40 °C resulted in 0.81 g (80%) of 2a.

X-ray Data Collection and Structure Solution of $[(CH_3C_5H_4)_2ZrNNCHPh]_2$ (4). A suitable crystal was grown from a toluene/hexane solution at room temperature. Crystals of $[(CH_3C_5H_4)_2ZrNNCHPh]_2$ are orthorhombic, space group $P2_12_12_1$, with a = 8.262 (3) Å, b = 19.441 (7) Å, c = 21.922 (9) Å, V = 3521 (2) Å^3, and d(calcd) = 1.47 g/cm^{-3} for Z = 4 ($C_{38}H_{40}N_4Zr_2\cdot{}^1/_2C_6H_{14}$, fw = 778.4 g). An orange crystal of dimensions 0.16 × 0.20 × 0.24 mm was mounted on a glass fiber. Intensity data were measured at lowered temperature (160 ± 3 K) on a Nicolet R3m diffractometer equipped with a graphite monochromater and Mo Kα radiation (λ = 0.71069 Å) utilizing an ω-scan technique with variable scan rates. The data were corrected for decay but not absorption ($\mu_{MoK\alpha}$ = 6.2 cm^{-1}). A total of 3513 independent reflections were measured for $2\theta < 50°$ of which 2996 unique data were considered to be observed [$F_o > 3.0\sigma(F_o)$]. The structure was solved by conventional heavy-atom

Table III. Products (% Yields[a]) of Reactions between 2a and a Series of Substrates, 6

substr	7	8
 6a	 (35)	 (35)
 6b	 (30; 1:1.3)	 (31)
 6c	 (27; 1.4:1)	 (31)
 6d	 (30)	 (42)
 6e	 (27)	 (38)
 6f	 (17)	 (44)
 6g	 (45)	 (36)

[a] By VPC; the remainder was unreacted starting material; ratios for olefins are *Z*:*E*. [b] δ 7.21 (m, 5), 6.10 (br s, 1), 2.58 (m, 1), 2.20 (m, 2), 1.8–1.2 (m, 6), 1.08 (d, *J* = 6.6 Hz, 3). [c] δ 7.22 (m, 5), 6.20 (br s, 1), 2.4–2.1 (m, 4), 1.8–1.2 (m, 5), 0.99 (m, 3). [d] δ 7.16 (m, 5), 6.15 (br s, 1), 2.2–1.1 (m, 10), 0.80 (d, *J* = 6.2 Hz, 6). [e] δ 8.24 (s, 1), 7.73 (m, 2), 7.41 (m, 3), 3.06 (m, 1), 2.39 (m, 2), 1.63 (m, 6), 1.19 (d, *J* = 6.8 Hz, 3). [f] δ 8.25 (s, 1), 7.66 (m, 2), 7.32 (m, 3), 2.37 (m, 4), 1.71 (m, 5), 0.94 (d, *J* = 4.2 Hz, 3); HRMS 214.465 (calcd 214.1469). [g] δ 8.25 (s, 1), 7.67 (m, 2), 7.31 (m, 3), 2.34 (m, 4), 1.78 (m, 5), 0.88 (d, *J* = 6.1 Hz, 3). [h] δ 8.28 (s, 1), 7.76 (m, 2), 7.38 (m, 3), 2.34 (m, 4), 1.69 (m, 6), 0.90 (d, *J* = 5.9 Hz, 6). [i] δ 8.33 (s, 1), 7.74 (m, 2), 7.42 (m, 3), 2.13 (m, 4), 0.92 (m, 5), 0.89 (s, 9); HRMS 230.1415 (calcd 230.1418).

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(21) Day, A. C.; Whiting, M. C. *Org. Synth.* **1970**, *50*, 3.

methods (Patterson and Fourier) and was refined by blocked-cascade least squares. All calculations were carried out using the SHELXTL program. In the final stages of refinement, anisotropic thermal parameters were used for the non-hydrogen atoms. The phenyl and cyclopentadienyl hydrogen atoms were located on a difference Fourier map and were entered at idealized positions. The methyl hydrogens were not located. The hydrogen atoms were assigned isotropic temperature factors of $B(\mathrm{H}) = 1.2B(\mathrm{C})$. A hexane molecule of solvation, located on a difference Fourier map and refined with isotropic thermal parameters, is disordered around the 2-fold screw axis in the x direction. At convergence, $R = 0.056$ and $R_w = 0.057$ for 2996 data and 409 variables.

Reactions of Metalloazine Complexes with Organic Carbonyl Compounds. a. Reaction of $[Cp_2ZrNNCHPh]_2$ (2a) with Cyclohexanone. To a solution of $[Cp_2ZrNNCHPh]_2$ (0.068 g, 0.10 mmol) in THF (2 mL) under argon was added cyclohexanone (12 μL, 0.095 mmol). The reaction was heated to 60 °C for 9 h. An aliquot (0.5 mL) was removed and hydrolyzed with a few drops of 5% KOH solution. The resulting pale yellow mixture was dried over K_2CO_3 and filtered through Florisil. The products were analyzed by GC and GC–MS, and their identities were confirmed by comparison with samples prepared according to published procedures.

b. Reaction of $[Cp_2ZrNNCHPh]_2$ with Cyclohexanone Derivatives. Reactions of $[Cp_2ZrNNCHPh]_2$ with the organic carbonyl compounds **6** shown in Table III were carried out using the procedure and conditions described above. Products were analyzed by GC (6-ft 3% OV-17 column). Characterization data (or literature references) for olefins **7** and mixed azines **8** are given in Table III. Condensation reactions using other zirconium metalloazines[28] were performed in similar fashion.

Determination of the Rate of Reaction between $[Cp_2ZrNNCHPh]_2$ (2a) and Cyclohexanecarboxaldehyde. To a solution of **2a** (0.040 M, 0.750 mL, 0.030 mmol) in C_6D_6 at 10 °C in a screw-capped NMR tube fitted with a Teflon septum was added dioxane (internal standard, 1.00 μL) and cyclohexanecarboxaldehyde (6.00 μL, 0.050 mmol). The reaction was monitored by NMR (Bruker, 250 MHz), programmed to store FID's at set time intervals. After 8 h, the NMR sample was removed from the probe and was allowed to reach room temperature. Tridecane was added as a GC standard, and the reaction mixture was worked up in the usual manner. Analysis by GC showed **7g** (36%) and **8g** (40%). NMR spectra were integrated relative to dioxane, and the areas obtained for $[Cp_2ZrNNCHPh]_2$, starting aldehyde, 1-phenyl-2-cyclohexylethene (**7g**), and α-((cyclohexylmethylene)hydrazono)toluene (**8g**) were analyzed (using DATA.FOR program).[28] The plot for

$$k_2t = \frac{1}{(B_0 - A_0)} \ln \frac{A_0(B_0 - X)}{B_0(A_0 - X)}$$

was found to be linear within the initial phase of the reaction for the formation of both olefin and azine (using a XKIN3.FOR program). Least-squares analysis of the first 90 min of the reaction gave k_2 (cc = correlation coefficient; int = intercept). (Data plots are available as supplementary material.)

$$\begin{array}{rl} \text{olefin } k_2 = 2.73 \times 10^{-2} & \text{azine } k_2 = 2.23 \times 10^{-2} \\ \text{cc} = 0.984 & \text{cc} = 0.964 \\ \text{int} = 1.47 \times 10^{-5} & \text{int} = 1.97 \times 10^{-5} \end{array}$$

Rates of reactions between metalloazine complexes **2a–d** and cyclohexanecarboxaldehyde and between complex **2b** and aldehydes **5a–d** were determined according to the procedure described above. Data plots for rate calculations are available as supplementary material.

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Registry No. **1a**, 100763-30-2; **1b**, 100789-89-7; **1c**, 100763-35-7; **1d**, 100763-36-8; **2a**, 104531-96-6; **2a**·$^1/_2C_7H_8$, 122844-61-5; **2b**, 104548-75-6; **2c**, 122844-58-0; **2d**, 122844-59-1; **3a**, 104531-97-7; **3b**, 122844-62-6; **3c**, 122844-63-7; **3d**, 122844-64-8; **4**, 104531-98-8; **4**·$^1/_2C_6H_{14}$, 104531-99-9; **6a**, 108-94-1; **6b**, 583-60-8; **6c**, 591-24-2; **6d**, 589-92-4; **6e**, 5432-85-9; **6f**, 98-53-3; **6g**, 2043-61-0; **7a**, 1608-31-7; (*Z*)-**7b**, 122822-39-3; (*E*)-**7b**, 122822-40-6; (*Z*)-**7c**, 122822-42-8; (*E*)-**7c**, 122822-43-9; **7d**, 92377-88-3; **7e**, 122822-46-2; **7f**, 122822-48-4; **7g**, 5700-45-8; **8a**, 35430-51-4; **8b**, 122822-41-7; **8c**, 122822-44-0; **8d**, 122822-45-1; **8e**, 122822-47-3; **8f**, 122822-49-5; **8g**, 104531-90-0; $MoO_2(S_2CNEt_2)_2$, 19680-83-2; $MoO(S_2CNEt_2)_2$, 25395-92-0; $MoO(S_2CNMe_2)_2$, 39587-09-2; Cp_2ZrCl_2, 1291-32-3; $PhHC(N_2)$, 766-91-6; $MePhC(N_2)$, 22293-10-3; $Ph_2C(N_2)$, 883-40-9; $Ph_3PCH(CH_2)_3CH_3$, 29541-98-8; $Ph_2CNNCH(CH_2)_3CH_3$, 122822-38-2; $H_2NN{=}CH(4\text{-}MeOC_6H_4)$, 5953-85-5; $H_2NN{=}CH(4\text{-}ClC_6H_4)$, 52372-80-2; $H_2NN{=}CH(4\text{-}NCC_6H_4)$, 87829-00-3; phenylhydrazone, 5281-18-5.

Supplementary Material Available: Analytical data for **1a–d** and **2a–f** and X-ray diffraction data, including selected bond distances, bond angles, and atomic coordinates and isotropic thermal parameters for **2a** and **4** and distances from mean planes for **4**, an ORTEP diagram for **2a**, and a representation of the unit cell for **4** (18 pages); tables of observed and calculated structural factors for **2a** and **4** (31 pages). Ordering information is given on any current masthead.

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