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Registry No. 1, 14694-95-2; 2, 13938-94-8; **4a**, 53450-79-6; **4b**, 70196-21-3; D-fructose, 57-48-7; furfuryl alcohol, 98-00-0; 1-deoxyerythritol, 4144-94-9; D-arabinitol, 488-82-4; D-sorbose, 87-79-6; 1-deoxythreitol, 122920-28-9; xylitol, 87-99-0; 1,3-dihydroxyacetone, 96-26-4; methane, 74-82-8; L-*glycero*-tetrulose, 533-50-6; glycerol, 56-81-5; ethanol, 64-17-5; 5-(hydroxymethyl)furfural, 67-47-0; 2-deoxy-D-glucose, 154-17-6; 1-(2-furanyl)-1,2-ethanediol, 19377-75-4; D-*manno*-2-heptulose, 3615-44-9; 2,7-anhydro-*manno*-2-heptulopyranose, 7739-21-1; 2,7-anhydro-*manno*-2-heptulofuranose, 122844-56-8; 5-(1,2-dihydroxyethyl)-2-furancarboxaldehyde, 98546-42-0; 2,7-anhydro-*altro*-2-heptulopyranose tetrakis(trimethylsilyl ether), 122844-57-9.

Synthesis and Electrophilic Properties of Neutral Molybdenum Formyl Complexes $Mo(C_5Me_5)(CO)_2(PR_3)CHO$: Access to Secondary Heterocarbene Compounds

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The neutral formyl complexes $MoCp^*(CO)_2(L)CHO$ (**3a**, L = CO; **3b**, L = $P(OPh)_3$; **3c**, L = PPh_3; **3d**, L = PPh_2Me; **3e**, L = PMe_3) are conveniently synthesized by sodium borohydride reduction of the corresponding metal carbonyl $[MoCp^*(CO)_3(L)^+PF_6^-$ (**2a–e**) in cold methanol. These thermally unstable species are isolated in 90% yield as a mixture of microcrystals of both cis and trans isomers, the selectivity (cis/trans) ranging from 10/90 (PPh_3) to 95/5 (PMe_3). The X-ray crystal structure of **3e** recorded at 128 K shows that it crystallizes in the monoclinic space $P2_1/c$ with unit cell parameters a = 14.580 (8) Å, b = 8.244 (12) Å, c = 15.991 (8) Å, β = 94.28 (5)°, and Z = 4. The structure was solved and refined (3402 reflections) to the final values for residual R = 0.051 and R_w = 0.044. The perpendicular orientation of the Cp* and CHO ligands evidenced from the crystal data is also assumed to be the favored conformation in solution, from the temperature dependence of the $^3J_{PH}$ coupling constants for the formyl proton resonance. Monitoring the thermal decomposition of the cis/trans mixture of the compounds **3b–e** by variable-temperature ^1H NMR experiments shows a greater stability for the cis isomers and an evolution to the related metal hydride complexes by specific loss of the ligand located trans with respect to the formyl group. Mechanistic implications of these features are discussed. The formyl complexes **3c** and **3d** undergo an electrophilic O-addition with CH_3SO_3F, CF_3CO_2H, and $Me_3SiOSO_3CF_3$ affording specifically the corresponding secondary oxycarbene complexes $[MoCp^*(CO)_2(L)(CHOR)]^+X^-$ (**4**, L = PPh_3, R = Me; **6**, L = PPh_3, R = H; **7**, L = PPh_2Me, R = $Si(CH_3)_3$) which are isolated for the more thermally stable compounds **4** and **7** and all fully characterized.

Introduction

Since the first synthesis, by an indirect route, of a formyl complex as reported by Collman and Winter,[1] many formyl transition-metal complexes have been obtained. These have attracted intense interest, especially in connection with synthesis gas chemistry.[2] The less stable neutral transition-metal formyl complexes have been prepared by hydride reduction of coordinated CO. The most detailed studies were performed by Graham,[4] Gladysz,[5] and Casey[6] on piano-stool CpRe carbonyl complexes. The key role of the solvent and of the Lewis acid associated with the hydridic reagent were emphasized in the preparation and

(1) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089. (c) Casey, C. P.; Neuman, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5375. Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (d) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545. Tam, W.; Wong, W, K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

(2) (a) Henrici-Olive, G.; Olive, S. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 3, pp 391–434. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (d) Muetterties, E. L.; Stein, J. J. *Chem. Rev.* **1979**, *79*, 479. (e) Ponec, V. *Catal. Rev.—Sci. Eng.* **1978**, *18*, 151. (f) Kung, H. *Catal. Rev.—Sci. Eng.* **1980**, *22*, 235. (g) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic: New York, 1984. (h) Rofer-De Poorter, C, K. *Chem. Rev.* **1981**, *81*, 447. (i) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(3) When we were submitting the manuscript, a related paper by Gibson and co-workers appeared. Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.

(4) (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (b) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9. (c) May, C. J.; Graham, . A. G. *J. Organomet. Chem.* **1982**, *234*, C49.

(5) (a) Tam, W.; Lin, G. Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525. (b) Tam, W.; Lin, G. Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (c) Gladysz, J. A.; William, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1. (d) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5608. (e) Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596.

(6) (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395. (b) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (d) Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3371.

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isolation methods of the formyl complexes; however, isolated neutral metal formyl compounds are still scarce.[3-12] Indeed, the low kinetic and thermodynamic stability of the metal formyl complexes,[3i] together with their strong hydride donor ability and their electrophile-induced disproportionation investigated by Gladysz,[5] considerably limits the range of study devoted to these difficult to handle species. This led us to investigate the synthesis, stability, and reactivity of a series of (pentamethylcyclopentadienyl)molybdenum formyl complexes with the main objective to find a new route to secondary heterocarbene complexes, the chemistry of which is limited due to the lack of synthetic routes. We have used the $MoCp^*(CO)_2(L)CHO$ ($Cp^* = \eta^5\text{-}C_5Me_5$) system, which offers several advantages. Although an homologous compound was already known for the cyclopentadienyl series,[9] the now well-known C_5Me_5 ligand has been choosen to protect the labile formyl and carbene fragments from competitive decomposition reactions. The methyl substituents are also used as a probe for NOE measurements.[13] Moreover, the molybdenum four-legged piano stool presents the advantage of a cis–trans isomerism; from comparison of the behavior of each isomer mechanistic information can be obtained.

In 1987, we reported the synthesis of $MoCp^*(CO)_2(PPh_3)CHO$ and its reactivity toward CH_3SO_3F and CF_3COOH.[14] We report here: (i) a convenient and stereoselective access to cis and trans isomers of the neutral formyl complexes $MoCp^*(CO)_2(L)CHO$ (**3a–e**) (L = CO, $P(OPh)_3$, PPh_3, PPh_2Me, PMe_3) and their spectral characterization; (ii) the X-ray crystal structure for one of these compounds (**3e**, L = PMe_3), (iii) a conformational analysis of the CHO ligand based on the temperature dependence of the $^3J_{PH}$ coupling constant; (iv) dynamic NMR studies of the stability of the cis and trans formyl isomers; and (v) the reactivity of these metal formyl species toward electrophilic reagents, which open an alternative route to the new secondary heterocarbene compounds.

Results and Discussion

1. Syntheses of $MoCp^*(CO)_2(L)CHO$ (3a, L = CO; 3b, L = $POPh_3$; 3c, L = PPh_3; 3d, L = $PMePh_2$; 3e, L = PMe_3). The molybdenum carbonyl cations $[MoCp^*(CO)_3L]^+PF_6^-$ (**2a**, L = CO; **2b**, L = $P(OPh)_3$; **2c**, L = PPh_3; **2d**, L = $PMePh_2$; and **2e**, L = PMe_3) were prepared from the readily available $MoCp^*(CO)_3H$ (**1a**), as previously reported (eq 1).[14] The molybdenum formyl complex

$$\underset{\mathbf{1a}}{MoCp^*(CO)_3H} + Ph_3C^+PF_6^- \xrightarrow[L]{CH_2Cl_2} \underset{\mathbf{2a-e}}{[MoCp^*(CO)_3L]^+PF_6^-} + Ph_3CH \quad (1)$$

$MoCp(CO)_2(PPh_3)CHO$ has been previously synthesized by sodium borohydride reduction of $[MoCp(CO)_3PPh_3]^+PF_6^-$ in methanol, and we adopt this procedure (eq 2).[9]

$$\underset{\mathbf{2a-e}}{[MoCp^*(CO)_3L]^+PF_6^-} + NaBH_4 \xrightarrow{CH_3OH} \underset{\mathbf{3a-e}}{MoCp^*(CO)_2(L)CHO} \quad (2)$$

We found that this synthesis is improved by carefully mixing, in the solid state, the cationic starting material with 5 equiv of sodium borohydride before the methanol is added at −80 °C. The metal carbonyl reactant dissolves between −70 °C (L = CO) and −20 °C (L = PMe_3) than the reaction takes place, depending on the electron-withdrawing character of the phosphorus ligand. The advantage of the methanol/sodium borohydride system comes from the selectivity of the reduction, which stops after the first hydride transfer affording the metal formyl complex as a single product. Moreover, the neutral molybdenum formyl compounds precipitate from the medium and can be isolated by filtration. Phosphine-substituted formyl compounds **3b–e** are isolated as yellow microcrystals in an average yield greater than 90%. Since they are stable only for a few minutes at room temperature, satisfactory elemental analysis has not been possible. However, the formyl complexes that are isolated in a spectroscopically pure form may be stored for several months at −20 °C. Despite the presence of 5–10% of $MoCp^*(CO)_3H$ (**1a**) as an impurity, the molybdenum compound **3a** is the first example of an isolated neutral transition-metal formyl complex that does not contain stabilizing phosphorus ligands.

The molybdenum formyl complexes **3a–e** are characterized by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopies. The IR spectrum (Nujol) of the carbonylmolybdenum formyl complex $MoCp^*(CO)_3CHO$ (**3a**) displays three carbonyl stretching bands at 2045, 1950, and 1650 cm^{-1}. The low-frequency IR stretching mode associated with the formyl carbon–oxygen bond decreases to approximately 1600 cm^{-1} for the phosphine-substituted derivatives **3b–e** and compares well with the data previously noted for neutral metal formyl compounds.[4a,5b,7b,8,9] The ^1H NMR spectrum (CD_3OD, −80 °C) of **3a** exhibits a low field singlet at δ 14.68 characteristic of the formyl proton. The substitution of an ancillary carbon monoxide group with a phosphine or a phosphite ligand does not change significantly the chemical shift value (see Experimental Section). However the ^1H NMR spectra of compounds **3b–e** present two sets of signals, showing the presence of a mixture of cis and trans isomers. In agreement with the literature data,[15] the cis isomers display a lower field doublet with a larger coupling constant, $^3J_{PH}$, for the formyl proton resonance relative to the trans isomers. Moreover, the chemical shifts of the C_5Me_5 protons are at a significantly lower field for the trans isomer than for the cis. The kinetic cis/trans ratio (see below), deduced from the ^1H NMR integrated spectra, increases from 10:90 (L = PPh_3) to 95:5 (L = PMe_3) with the electron-withdrawing property of the phosphine ligands. In the case of the triphenyl phosphite ligand the cis/trans isomer ratio is 50:50.

Carbon-13 NMR studies confirm the existence of two isomers. In the 75-MHz proton-coupled ^{13}C NMR spectra, the formyl carbon atoms appear as two characteristic double doublets around 280 ppm with a large $^2J_{PC}$ coupling constant for the cis compound and a smaller value for the trans. The $^1J_{CH}$ coupling constants are similar for the two isomers. The magnetically equivalent CO ligands of the trans isomers resonate as a single doublet with a $^2J_{PC}$ value around 30 Hz. In the cis isomers, the metal center is chiral;

(7) (a) Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430. (b) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1988**, *7*, 1683.
(8) (a) Nelson, G. O. *Organometallics* **1983**, *2*, 1474. (b) Nelson, G. O.; Summer, C. E. *Organometallics* **1986**, *58*, 1983.
(9) Gibson, D. H.; Owens, K.; Ong, T.-S. *J. Am. Chem. Soc.* **1984**, *106*, 1125.
(10) (a) Leoni, P.; Landi, A.; Pascuali, M. *J. Organomet. Chem.* **1987**, *321*, 365. (b) Leoni, P.; Aquini, E.; Pascuali, M.; Marchetti, F.; Sabat, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 329.
(11) (a) Berke, H.; Huttner, G.; Weiller, G.; Zoolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353. (b) Berke, H.; Huttner, G.; Scheidst, E. O.; Weiller, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 735. (c) Berke, H.; Kundel, P. *Z. Naturforsch., B* **1986**, *41B*, 527.
(12) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.
(13) Guerchais, V.; Lapinte, C.; Thépot, J.-Y. *Organometallics* **1988**, *7*, 604.
(14) Asdar, A.; Lapinte, C. *J. Organomet. Chem.* **1987**, *327*, C33.

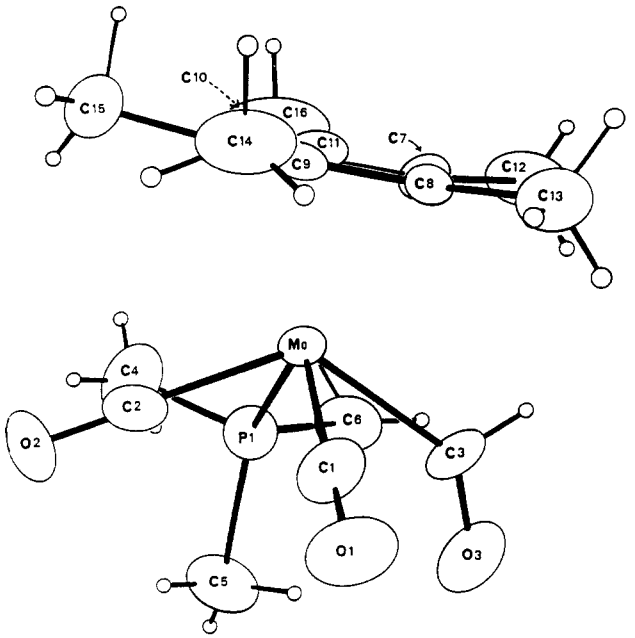


Figure 1. An ORTEP representation of *cis*-$Mo(C_5Me_5)(CO)_2(PMe_3)CHO$ (*cis*-**3e**).

Table I. Selected Bond Distances and Angles for $Mo(C_5Me_5)(CO)_2(PMe_3)CHO$ (3e)

Bond Distances (Å)			
Mo–P(1)	2.462 (2)	C(1)–O(1)	1.147 (7)
Mo–C(1)	1.962 (7)	C(2)–O(2)	1.176 (7)
Mo–C(2)	1.955 (6)	C(3)–O(3)	1.212 (7)
Mo–C(3)	2.156 (6)		
Mo–C_5Me_5 (centroid)	2.031 (6)		

Bond Angles (deg)			
P(1)–Mo–C(1)	113.0 (2)	Mo–C(1)–O(1)	177.9 (6)
P(1)–Mo–C(3)	75.5 (2)	Mo–C(2)–O(2)	178.8 (6)
C(1)–Mo–C(2)	76.4 (3)	Mo–C(3)–O(3)	138.2 (5)
C(1)–Mo–C(3)	71.2 (3)	Mo–C(3)–O(3)–H(3)/C_5Me_5	84.6 (4)
C(2)–Mo–C(3)	124.0 (3)		

the two carbonyl groups are diastereotopic and resonate as a doublet attributed to the carbonyl cis with respect to the phosphorus ligand and a singlet corresponding to the carbonyl in trans geometry with respect to this ligand.[15]

2. Crystal and Molecular Structure of $MoCp^*(CO)_2(PMe_3)CHO$ (3e). Yellow crystals of *cis*-**3e** were obtained by recrystallization from toluene/pentane at −40 °C, and the single-crystal X-ray structure was determined at 128 K. The unit cell contained four molecules of *cis*-**3e** and two molecules of methanol. Note that crystallization in cold ether eliminated the solvent used in the synthesis, but no suitable crystals could be obtained for X-ray diffraction. The formyl ligand was found to be in a cis geometry with respect to the phosphine as shown by the ORTEP representation (Figure 1). Selected bond distances and angles are listed in Table I. The molecule may be

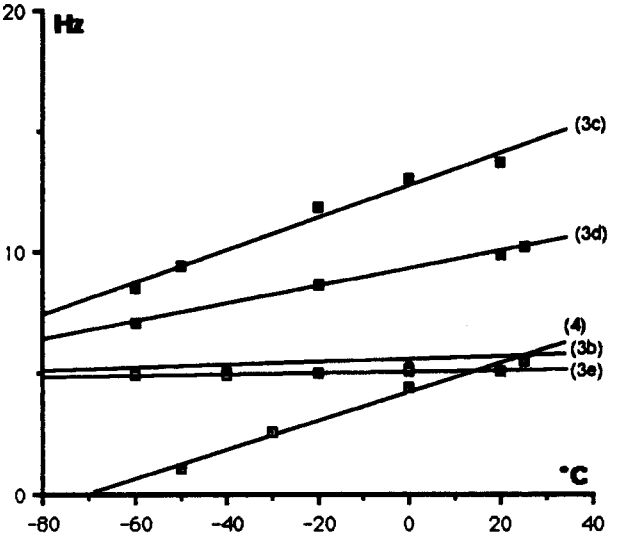
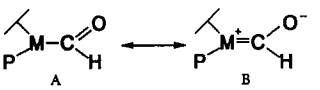


Figure 2. $^3J_{PH}$ coupling constants vs temperature for the formyl (**3b–e**) and methoxycarbene (**4**) compounds.

Scheme I

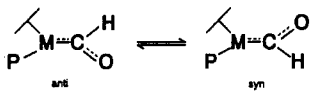


formally regarded as a seven-coordinate molybdenum complex with the pentamethylcyclopentadienyl ligand occupying three coordination sites. The cyclopentadienyl ring is planar to within 0.002 Å, and the methyl carbon atoms are above this plane and away from the molybdenum atom an average of 0.14 (1) Å, ranging from 0.08 (1) to 0.19 (1) Å. The distance of the Mo atom to the centroid of the Cp* ring of 2.031 (6) Å is the same as that found earlier in the MoCp* series.[19] The two carbonyl groups, the trimethylphosphine, and the formyl ligands occupy the other four sites. The trans C(2)–Mo–C(3) and C(1)–Mo–P(1) angles are 124.0 (3) and 113.0 (2)° while the cis angles C(1)–Mo–C(2), C(1)–Mo–C(3), C(3)–Mo–P(1), and C(2)–Mo–P(1) are between 70.6 and 77.0°, as expected for a four-legged piano-stool geometry.[16-18]

The major focus of interest is on the structural features of the formyl ligand. The relevant parameters are the Mo–C(3)–O(3) angle (138.2 (5)°) and the location of the formyl hydrogen atom oriented toward the cyclic C_5 ligand. The metal atom and the three CHO formyl atoms are coplanar; this plane and the Cp* ring being almost perpendicular (84.6°). The resultant inequivalence of the coordinated CO molecules is not seen in the X-ray crystal data. However, the formyl carbon–metal bond distance is significantly longer than the metal–carbonyl bond length. In light of discussions by other groups on the structure of formyl complexes, several other points are worth noting. The orientation of the formyl oxygen atom toward the cyclic ligand has been reported for $ReCp(PPh_3)(NO)(CHO)$,[5] while the opposite orientation is observed for $RuCp^*(CO)(PMe_2Ph)CHO$.[8] The formyl C=O bond length, 1.212 (7) Å, is close to the 1.220 (12) Å value found by Gladysz and co-workers[5] and is somewhat longer with respect to other values.[8,20-22] These observations parallel

(15) Asdar, A.; Tudoret, M. J.; Lapinte, C. *J. Organomet. Chem.* **1988**, *349*, 353.
(16) Wilford, J. B.; Whitla, A.; Powell, H. M. *J. Organomet. Chem.* **1972**, *44*, 1.
(17) For $CpMo(CO)_3$ see (inter alia): (a) Salnikova, T. N.; Andrianov, V. G.; Struchkov, Yu. T. *Koord. Khim.* **1976**, *2*, 707. (b) Rajaram, J.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 1313. (c) Deutscher, J.; Fadel, S.; Ziegler, M. *Angew. Chem.* **1977**, *89*, 746. (d) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6326. (e) St. Denis, J.; Butler, W.; Glick, M. P.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5427. (f) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197. (g) Bir'yukov, B. P.; Struchkov, Yu. T.; Anisimov, K. N.; Kolobova, N. E.; Beschastnov, A. S. *J. Chem. Soc., Chem. Commun.* **1968**, 667.
(18) Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1061.
(19) Leoni, P.; Grilli, E.; Pasquali, M.; Tomassini, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1041.
(20) Casey, C. P.; Meszaros, M. W.; Neumann, S. M.; Cesa, I. G.; Haller, K. J. *Organometallics* **1985**, *4*, 143.
(21) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302.

Scheme II



the low IR stretching frequency associated with the low-field ^{13}C NMR observed for the carbon formyl atom and indicate a carbon–oxygen bond order lower than 2 for the carbon–oxygen bond. This feature is a consequence of the contribution of the mesomeric form B (Scheme I) as already mentioned.[5,21]

The favored perpendicular orientation of the formyl group with respect to the cyclic ring is significant for this trend and indicates a partial double character for the metal–carbon bond. Hoffmann has predicted from Hückel MO calculations similar ground-state conformation for the methylene complex $[MoCp^*(PH_3)(CO)_2(=CH_2)]^+$.[2,3] Moreover the perpendicular conformation has also been observed for structurally similar heterocarbenes complexes.[26,27] As already noted for the related rhenium chemistry,[5b] the formyl ligand adopts a carbene geometry.

3. Conformational Analysis. The ^1H NMR spectra of the formyl complexes recorded from −50 °C to 25 °C show an increase of the $^3J_{PH}$ coupling constant between the formyl proton and the phosphorus atom with increasing temperature for the trans isomers (Figure 2). These variations are especially important for the compounds *trans*-**3c** (L = PPh_3) and *trans*-**3d** (L = $PMePh_2$). The favored perpendicular conformation adopted by the formyl group gives rise to the syn and anti conformers for the molybdenum formyl complexes (Scheme II). Lesser steric crowding in the anti conformation corresponds to greater thermodynamic stability of the latter, which is observed in the crystal structure.

The observation of only one set of resonances in the NMR spectrum of each compound suggests that the barrier of rotation about the M–C bond is sufficiently low that the interconversion between the syn and anti rotamers is rapid on the ^1H NMR time scale and only the time-averaged spectra are being observed. Therefore, the variation of the $^3J_{PH}$ values indicates that the relative conformer populations are changing with temperature.[24,25] Furthermore, on the basis of the NMR parameters of the iron and tungsten methylene compounds reported by Brookhart et al., it can be assumed that the $^3J_{PH}$ coupling constant between the anticlinal proton and the phosphorus atom (Scheme II, form C) is substantially greater than the coupling constant between the synclinal proton and the phosphorus atom (form D).[26,27] The increase of the $^3J_{PH}$ values with the temperature can be rationalized in terms of a Boltzmann distribution over the anti ground state and the syn rotamers.

It is noteworthy that the trans isomer of the parent secondary methoxycarbene compound $[MoCp^*(CO)_2(PPh_3)CHOMe]^+PF_6^-$ (**4**) (see below) exhibits the same behavior for the $^3J_{PH}$ coupling constant (Figure 2) which

Table II. Nuclear Overhauser Effect (FID Difference NOE Experiments) Observed on the CHO Proton upon Irradiation of the C_5Me_5 Methyl Groups of $Mo(C_5Me_5)(CO)_2(L)CHO$ (3b–e)

complex	L	T, °C	cis/trans	
3b	$P(OPh_3)$	−30	**26**	21
3c	PPh_3	−80		12
3d	PPh_2Me	−20	19	12
3e	PMe_3	−60	22	

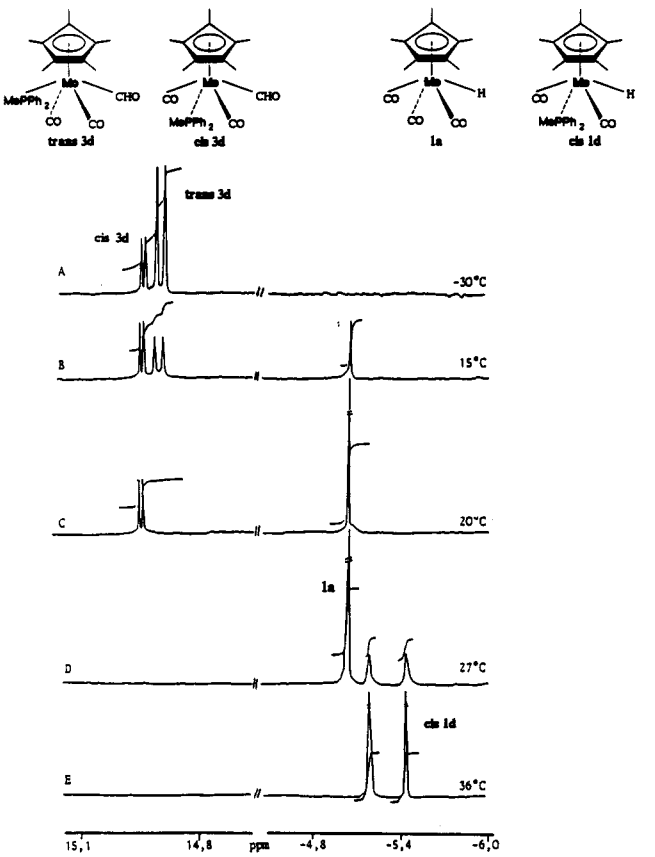


Figure 3. Variable-temperature 300-MHz ^1H NMR spectra of *cis*- and *trans*-**3d** in toluene-d_8.

emphasizes again the structural analogy between organometallic formyl and carbene complexes. Irradiation of the proton C_5Me_5 resonance results in a large enhancement of the formyl proton resonance for both cis and trans isomers (Table II). These results provide additional evidence for short distance interactions between the bulky permethylated C_5 ring and the formyl ligand[13,28] and indicate a steric protection of the labile formyl hydrogen atom.

4. Thermal Stability Studies of $MoCp^*(CO)_2(L)CHO$. Complex **3a**, more soluble in methanol than the substituted formyl compounds **3b–e**, cannot be isolated from the reaction medium. Indeed, it decomposes at −20 °C in about 10 min to form the metal hydride **1a**. Complexes **3b–e** are stable in a degassed solution of benzene or toluene up to 10 °C; above this temperature they decompose to *cis*-$MoCp^*(CO)_2(L)H$ (**1b**, L = $P(OPh)_3$; **1c**, L = PPh_3; **1d**, L = $PMePh_2$; **1e**, L = PMe_3)[30] which are recovered in a quantitative yield after 72 h at room tem-

(22) (a) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 387. (b) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2501.

(23) Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

(24) (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292. (b) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522. (c) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. M.; Whittaker, M. *J. Am. Chem. Soc.* **1987**, *109*, 5711.

(25) Karplus, J. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

(26) Klegey, S. E.; Brookhart, M. *Organometallics* **1982**, *1*, 760.

(27) Brookart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1986**, *5*, 947.

(28) The spatial proximity between the methyl group of the C_5Me_5 ligand and the formyl hydrogen atom should be shorter than 2.5 Å in solution so a NOE could be observed.[29] In the single-crystal structure of **3e** this distance was measured as 1.98 Å.

(29) Schirmer, R. E.; Noggle, J. *J. Am. Chem. Soc.* **1972**, *94*, 2947.

(30) Tudoret, M. J.; Lapinte, C., work in progress.

perature (eq 3). Addition of 9,10-dihydroanthracene, a

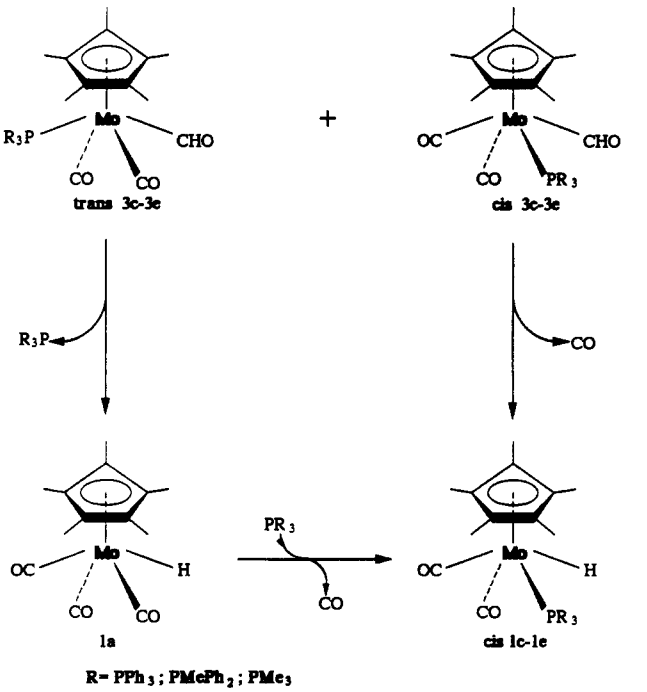
$$\underset{cis\text{-}+\ trans\text{-}\mathbf{3b-e}}{MoCp^*(CO)_2(L)CHO} \xrightarrow{-CO} \underset{cis\text{-}\mathbf{1b-e}}{cis\text{-}MoCp^*(CO)_2(L)H} \quad (3)$$

hydrogen atom donor, to solutions of the formyl complexes does not stabilize them, indicating that the thermal decomposition of these compounds does not proceed through an electron-transfer pathway with an homolytic cleavage of the carbon-to-hydrogen bond of the formyl group as already noted.[8,31]

The thermal decomposition of the formyl complexes has been monitored in variable-temperature ^1H NMR experiments. Their behavior depends on the presence of either a phosphine or a phosphite group at the molybdenum center. In the case of the phosphine-substituted formyl compounds, the PPh_2Me derivative is optimal for observation of the stepwise conversion into metal hydride complexes. As illustrated in Figure 3, the ^1H NMR spectrum ($C_6D_3CD_3$) of the cis–trans mixture of $MoCp^*(CO)_2(PMePh_2)CHO$ (**3d**), recorded between −30 °C and +36 °C, is representative of the evolution of the phosphine-substituted formyl compounds. The first spectrum (−30 °C) displays two doublets (δ 14.98 and 14.91), corresponding, respectively, to the cis and trans isomers of the formyl complexes free of any trace of hydride. As the temperature rises, decomposition takes place. The signal due to the hydride $MoCp^*(CO)_3H$ (**1a**) (δ −5.08) appears and increases while the doublet attributed to the *trans*-**3c** formyl compound decreases.[9] The spectrum recorded at 20 °C shows that decomposition is complete. The more stable cis isomer neither converts into the metal hydride derivative nor isomerizes to the trans homologue below 20 °C. At higher temperature (27 °C), it decompose to *cis*-$MoCp^*(CO)_2(PMePh_2)H$ (*cis*-**1d**) over a 1-h period. The free phosphine ligand (PPh_2Me), lost by *trans*-**3d**, reacts more slowly (24 h, 25 °C) with $MoCp^*(CO)_3H$ to afford the hydride *cis*-**1d**.[32] The stepwise decomposition of **3c** (L = PPh_3) and **3e** (L = PMe_3) follows the same trend as **3d**, with a weak increase of the stability order from PPh_3 to PMe_3. However, we note the large and unexpected stability of *cis*-**3c**, which is stable at 50 °C for several hours.

Finally, each metal formyl isomer separately decomposes by specifically losing the trans ligand (with respect to the formyl group). A straightforward mechanism that accommodates all these observations is outlined in Scheme III. The stereospecificity of the decomposition reaction is not consistent with the loss of the formyl CO group, as expected for the reverse mechanism of the thermodynamically unfavored CO insertion into the metal–hydrogen bond. Indeed, although the migratory insertion of CO into a metal–hydrogen bond to produce formyl has been much discussed as a primary event in the heterogeneous catalytic hydrogenation of carbon monoxide and has been the subject of theoretical studies, there is little umambiguous evidence for this reaction with model compounds.[21,33,34] However such an insertion has been nicely established for organoactinide hydrides, the driving force being then the formation of the metal–oxygen bonds.[35]

Scheme III



Since added triphenylphosphine is found to slow the conversion of the more labile formyl compound $MoCp(CO)_2(PPh)_3CHO$,[9a] we examined the influence of trimethylphosphine (a better donor ligand than $PMePh_2$) on the thermal evolution of **3d**. No trace of the ligand-exchanged formyl complex **3e** could be detected, and the behavior of both cis and trans isomers was not modified. Furthermore, the decomposition rate does not depend either on the concentration of free phosphine in the solvent or on the concentration of the formyl complex. Only a mixture of hydride compounds *cis*-**1d** and *cis*-**1e** is obtained, due to a competitive carbonyl exchange from $MoCp^*(CO)_2H$[32] (**1a**). These data are consistent with a mononuclear formyl decomposition consisting of hydride migration from the formyl group to the metal. Extrusion of the trans ligand would be concerted with the hydride migration and is easier for a better π acceptor.

The ^1H NMR spectra that monitor the decomposition of $MoCp^*(CO)_2(P(OPh)_3)CHO$ (**3c**) show an evolution which is rather different from its phosphine-substituted relatives. The different behavior comes from the interconversion between the cis and trans formyl isomers. Indeed, the cis/trans isomers of the formyl compound **3c** in toluene solution are stable up to 20 °C and decompose slowly above this temperature, specifically affording $MoCp^*(CO)_3H$ (**1a**) and the free phosphite. However the cis/trans ratio remains unchanged (50:50), indicating a conversion of the cis formyl isomer into the trans one. (The decomposition of both cis and trans formyl isomers **3c** with the specific loss of the phosphite ligand at the same rate is highly unlikely.) This result indicates that the two formyl isomers of **3c** are in thermodynamic equilibrium with the same energy (Scheme IV). This feature prevents the determination of the kinetic stability of *cis*-**3c**, but we can observe that the *trans*-**3c** compound is as stable as the PMe_3-substituted formyl complex *trans*-**3e**. The weaker electron donor ability of the phosphite relative to the

(31) (a) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351. (b) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139. (c) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1984**, *3*, 802.

(32) Analogous observations were done in $(C_5H_5)Mo$ series. Bainbridge, A.; Craig, P. J.; Green, M. L. H. *J. Chem. Soc. A* **1968**, 2715.

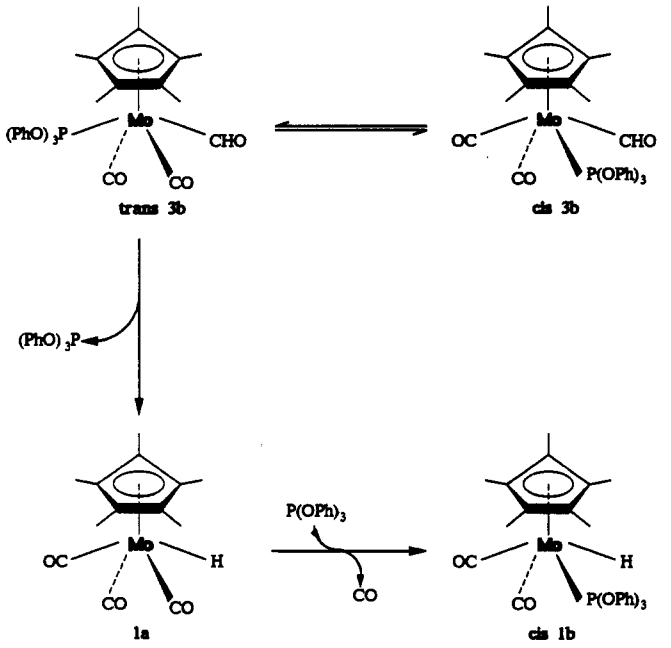
(33) For theoretical aspects, see: Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7724.

(34) (a) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700. (b) Davies, S. G.; Simpson, S. J. *J. Organomet. Chem.* **1982**, *240*, C8. (c) Davies, S. G.; Hiblerd, J.; Simpson, J. J.; Thomas, S. E.; Watts, O. *J. Chem. Soc., Dalton Trans.* **1983**, 1805.

(35) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.

(36) Vollhardt, K. P. C. *Organic Chemistry*; W. H. Freeman: New York, 1987; pp 399–405.

Scheme IV



phosphine is balanced by its strongerer π-acceptor ability to stabilize the formyl complexes.

5. Stereoselectivity of the $NaBH_4$ Reduction of $[MoCp^*(CO)_3PR_3]^+PF_6^-$. The noninterconversion between the cis and trans formyl isomers (L = $POPh_3$) implies that the cis–trans ratio of the isolated formyl compounds are kinetic in origin. The rates of the nucleophilic hydride attack are different at the two cis carbonyl groups and at the single trans CO ligand with respect to the phosphorus atom of the cationic precursors, and the ratio of the rate constants is determined by eq 4.

$$\log\{[\text{cis}]/2[\text{trans}]\} = \log(k_{cis}/k_{trans}) \quad (4)$$

The linear relationship observed between the kinetic rate constants and the ^{13}C NMR chemical shifts of the CO ligands (Figure 4) illuminate the control of the stereoselectivity of the sodium borohydride reduction of the cationic $[MoCp^*(CO)_3PR_3]^+PF_6^-$ complexes by the electronic properties of the phosphine ligands. Since the chemical shift of a carbon nucleus reflects, at least in part, for an homologous family of compounds, the electron density at the carbon atom. Note that the hydride reduction of **3b** (L = $P(OPh)_3$) deviates from this relationship, since in this case the cis/trans selectivity is thermodynamically controlled.

6. Reaction of 3c (L = PPh_3) with CH_3SO_3F. Synthesis of $[MoCp^*(CO)_2(PPh_3)(CHOMe)]^+PF_6^-$ (4). The alkoxy–alkyl and (alkyl)thio–alkyl complexes are potential precursors of carbene complexes. Indeed, the α-hydrogen and the hetero group are reactive toward abstracting reagents such as the trityl cation. Depending on the nature of the ancillary ligands coordinated to the metal center, the reaction leads chemospecifically to the corresponding hetero-substituted carbene complex or to the alkylidene species (eq 5).[5b,13,37,38] Since there are no generally useful

$$M\text{–}CH_2OR + Ph_3C^+PF_6^- \rightarrow \begin{cases} [M{=}CHOR]^+PF_6^- \\ [M{=}CH_2]^+PF_6^- \end{cases} \quad (5)$$

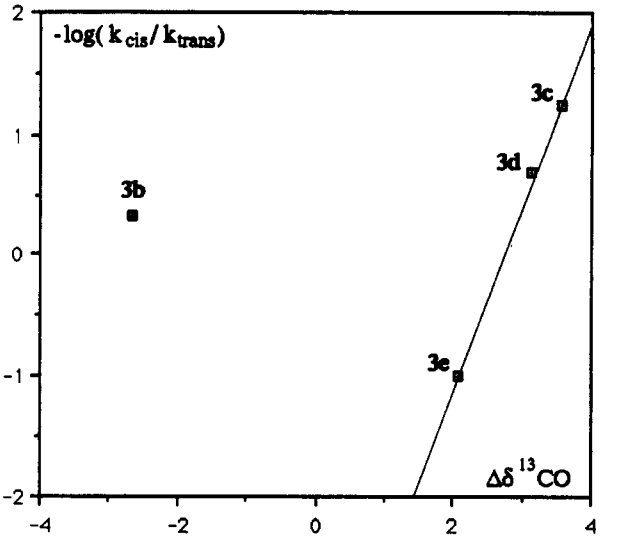


Figure 4. The ratio of the formation rate constants for the cis and trans formyl isomers vs the difference of the ^{13}C chemical shifts for the cis and trans carbonyl groups of the starting cations.

route to secondary heterocarbene complexes, reaction of the neutral molybdenum formyl complexes with electrophilic reagents was investigated with the ultimate goal of effecting a O-methylation. This has ample precedent in the case of the transition-metal acyl,[39] but in this system, it is still a challenge because of the electrophile-induced disproportionation of the neutral metal formyl complexes, as nicely established by Gladysz and co-workers.[5b,40]

The secondary methoxycarbene complex $[MoCp^*(CO)_2(PPh_3)(CHOMe)]^+PF_6^-$ (4) is readily synthesized by treatment of a low-temperature (−90 °C) methylene chloride solution of the formyl derivative **3c** with 1 equiv of CH_3SO_3F. After metathesis and recrystallization from a chloroform/pentane mixture, the methoxycarbene compound 4 is isolated as a thermally stable yellow solid in 60% yield[41] (eq 6). The molybdenum carbene complex

$$\underset{\textbf{3c}}{[M]\text{—}CHO} + CH_3SO_3F \xrightarrow[NH_4PF_6]{-90\ C} \underset{\textbf{4}}{[M]^+{=}CHOMePF_6^-} \quad (6)$$

$$[M] = MoCp^*(PPh_3)(CO)_2$$

4 is characterized by IR and ^1H, ^{31}P, and ^{13}C NMR spectroscopies. The ^1H spectrum ($CDCl_3$, 20 °C) of 4 exhibits two low-field doublets at δ 12.45 ($^3J_{PH}$ = 5.5 Hz) and 12.52 ($^3J_{PH}$ = 1.5 Hz) due to the carbene proton of the trans and cis isomers, respectively.[41] The other signals corresponding to the methoxy group are located at δ 4.02 and 4.80 for the trans and cis forms, respectively. These ^1H chemical shifts compare well with those reported by Brookhart for the related complex $[MoCp^*(CO)_2(PPh_3)(CHOMe)]^+SO_3CF_3^-$ generated in low yield by hydride abstraction from the corresponding methoxymethyl

(37) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (c) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

(38) (a) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604. (b) Constable, J. A.; Gladysz, J. A. *J. Organomet. Chem.* **1980**, *202*, 121. (c) Kegley, M.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (d) Knors, C.; Kuo, G. H.; Lauher, J. W.; Eigenbrot, C.; Helquist, P. *Organometallics* **1987**, *6*, 988.

(39) (a) Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* **1975**, *88*, 199. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (c) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764.

(40) Electrophilic addition on cationic metal formyl complexes were already performed and afforded the expective dicationic carbene compounds: (a) Barrat, D. S.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1987**, *327*, C33. (b) Ligla, M. A.; Ibers, J. A. *Organometallics* **1985**, *4*, 590.

(41) Note that the cis/trans ratio of 4 depends on the workup and recrystallization conditions (see Experimental Section).

derivative.[26] The ^{13}C resonances of the carbene carbon atom of both isomers at δ 339.33 (cis, $^2J_{CP}$ = 25.4 Hz) and 330.58 (trans, $^2J_{PC}$ = 6.6 Hz) confirm the proposed structure. The CO ligands exhibit a similar pattern to the parent formyl compound **3c** (i.e. a single doublet located at δ 227.87 ($^2J_{PC}$ = 30.5 Hz) for the trans isomer and two doublets at δ 235.81 ($^2J_{PC}$ = 29.7 Hz) and 233.62 ($^2J_{PC}$ = 4.0 Hz) for the two magnetically unequivalent CO groups of the cis isomer).

The successful generation of a secondary heterocarbene complex by direct O-alkylation of a metal formyl precursor requires that the hydridic formyl compound be stable enough to avoid in situ hydride transfer to the electrophilic carbene derivative formed. This aspect of the reactivity was carefully examined. Proton NMR monitoring of a CD_2Cl_2 solution containing a stoichiometric amount of the cis/trans isomers of the methoxycarbene complex **4** and the formyl compound **3c** between −90 °C and 20 °C showed no traces of the cationic complex **2c** and the alkoxymethyl derivative **5**, which would result from an intermolecular hydride-transfer reaction (eq 7). When the

$$\underset{\mathbf{3c}}{[M]\text{—}CHO} + \underset{\mathbf{4}}{[M]^+\text{=}CHOMe} \rightarrow \underset{\mathbf{2c}}{[M]^+\text{—}CO} + \underset{\mathbf{5}}{[M]\text{—}CH_2OCH_3} \quad (7)$$

$$[M] = MoCp^*(CO_2)(PPh_3)$$

temperature reached −20 °C, the slow decomposition of the formyl compound **3c** is observed, as mentioned above. Moreover, the O-methylation reaction of **3c** has also been monitored by variable-temperature ^1H NMR experiment, and the reaction is instantaneous and spectroscopically quantitative at −90 °C. It gives a mixture of the cis and trans isomers of the methoxycarbene **4** in the same ratio as the starting formyl complex **3c**, and any further isomerization was never observed. The chemical selectivity is dramatically changed by replacing the $CH_3SO_3CF_3$ reagent with the bulky trityl salt $Ph_3C^+PF_6^-$. In the latter case the cationic complex **2c** is specifically recovered as already described for the Cp homologous complex (eq 8).

$$\underset{\mathbf{3c}}{[M]\text{—}CHO} + Ph_3C^+PF_6^- \rightarrow \begin{cases} \not\rightarrow\ [M]^+\text{=}CHOCPh_3PF_6^- \quad (<1\%) \\ \rightarrow\ \underset{\mathbf{2c}\ (99\%)}{[M]^+\text{—}CO} + Ph_3CH \end{cases} \quad (8)$$

$$[M] = MoCp^*(CO)_2(PPh_3)$$

The selectivity also depends on the electronic properties of the formyl compounds, as controlled by the ligands coordinated to the metal center. Thus, with L = PPh_3 (or PPh_2Me, see below) the formyl complexes **3c** and **3d** are easily alkylated with a strong electrophilic reagent, whereas the more hydridic formyl compounds **3b** (L = $P(OPh_3)$) and **3e** (L = PMe_3) give no traces of a carbene complex. The latter reaction affords after workup, the cationic complex **2e** and the neutral ether compound $Mo(C_5Me_5)(CO)_2(PMe_3)CH_2OCH_3$ (**8**), which are recovered in 50% and 45% yields, respectively (eq 7). These compounds result from an in situ hydride-transfer reaction as earlier evidenced in the rhenium chemistry.[5b]

Our results establish that the metal formyl alkylation reaction can be an alternative synthetic route to secondary alkoxycarbene compounds. However this reaction requires a stabilized metal formyl complex with a low hydridic character as starting material and provide a secondary alkoxyalkyl carbene metal compound with a phosphorus ligand. This behavior is particularly interesting because the hydride abstraction from electron-rich alkoxyalkyl

Scheme V

precursors often fails affording either the methylene compound by alkoxyde abstraction[42] or byproducts through an electron-transfer pathway. Indeed the trityl salt, the more common hydride abstracting reagent, is also an efficient oxidizing agent, and electron-transfer reactions occur when the metal atom is coordinated to electron donor ligands.[45,46] Since our first communication on this new access to heterocarbene compounds,[14] the synthetic potential of this reaction was nicely illustrated by Gibson's group to prepare $[Mn(CO)_3(PPh_3)(=CHOMe)]^+$.[47] Our own investigations were directed toward the preparation of new complexes with functional secondary carbene ligands.

7. Synthesis of Secondary Hydroxy- and Siloxycarbene Complexes $[MoCp^*(CO)_2(L)(=CHOE)]^+X^-$ (6, L = PPh_3, E = H; 7, L = $PMePh_2$, E = $SiMe_3$). The reaction of **3c** with CF_3COOH in CD_2Cl_2 has been monitored by NMR at −70 °C. The direct protonation product of **3c** is quantitatively formed, and on the basis of both ^1H and ^{13}C NMR data the cis and trans hydroxycarbene structures $[MoCp^*(CO)_2(PPh_3)(CHOH)]^+CF_3COO^-$ (**6**) have been assigned. The starting formyl and hydroxycarbene complexes have the same cis/trans isomer ratio (10:90). The proton of the hydroxy group resonates as a broad singlet at δ 9.27, and the two low-field doublets at δ 13.20 (cis) and 12.99 (trans) are characteristic of the carbene proton resonances. The ^{13}C resoance of the carbene carbon atom located at δ 307.78 (due to the trans isomer, since the concentration of the cis isomer is too low to be detected) confirms the proposed structure. This value is somewhat lower than that of the chemical shift observed for complex **4** but is slightly higher than that already noted for the rhenium complex $[Re(Cp)(NO)(PPh_3)(=CHOH)]^+X^-$, the only other monocationic hydroxycarbene transition-metal compound to be characterized by ^{13}C NMR.[5b] Indeed, the hydroxycarbene fragment (=CHOH) is a very unusual two-electron ligand,[48] to date only three other bicationic related compounds have been reported with a Ru, Os, and Ir metal center.[40] Although compound **6** was stable in methylene chloride over a 1-day period at room temperature, its attempted isolation failed even with the use of a stronger acid like CF_3SO_3H.

The new secondary siloxycarbene compound $[MoCp^*(CO)_2(PPh_2Me)(=CHOSiMe_3)]^+SO_3CF_3^-$ (**7**) is prepared by addition of 1 equiv of $Me_3SiO_3SCF_3$ to a CH_2Cl_2 solution of **3d** at 0 °C. Compound **7** isolated as a spectroscopically pure red oil in 80% yield is stable over a half-day period at 20 °C and may be stored for 1 or 2 weeks at −20

(42) The hydride abstraction has been achieved by treatment of $Fe(C_5Me_5)(CO)(L)CH_2OCH_3$ with the trityl salt for L = CO, whereas the methoxide abstraction occurred when L = PPh_3.[43] The same trend has already been observed in other series.[5b,44]

(43) Guerchais, V.; Lapinte, C., unpublished work.

(44) Davies, S. G.; Seeman, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 6522.

(45) Reaction of *cis*-$Mo(C_5Me_5)(CO)_2(PPh_2Me)CH_2OCH_3$ with $Ph_3C^+PF_6^-$ proceeds through an electron pathway and does not afford the expected secondary carbene compound. Tudoret, M. J.; Lapinte, C., work in progress.

(46) (a) Roger, C.; Toupet, L.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1988**, 714. (b) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663.

(47) Mandal, S. K.; Owens, K.; Richardon, J. F.; Gibson, D. H. *Organometallics* **1987**, *6*, 2624.

(48) More highly substituted hydroxycarbene complexes have also been reported previously. For a pioneering example see: Green, M. L. H. *J. Organomet. Chem.* **1967**, *10*, 188.

°C. The ^1H NMR spectrum of **7** establishes that the cis and trans isomers are in the same ratio as that of the formyl parent compound **3d** (30:70). Two resonances at δ 0.01 and 0.02 suggest the presence of the Me_3Si fragment, and the carbene proton signals are observed at δ 12.80 and 13.15. The carbene carbon atom of both cis and trans isomers resonantes as a single broad signal at δ 341.69, indicating that the electronic structure of the carbene compounds **4** and **7** are very similar. The electrophilic character of the metal carbene fragment should be stronger in these compounds than in the hydroxycarbene derivative **6**, as shown by the upfield shift of ca. δ 30 (Scheme V).

The O-alkylation of metal formyl complexes can be an alternative route to novel secondary alkoxycarbene fragments, especially useful when the hydride abstraction reaction fails. This reaction is very sensitive to change in electronic environment about the metal center; thus we were unable to generate a carbene derivative from compound **3e**, and the electrophilic-induced disproportionation of the metal formyl complexes is an important competitive reaction. Nevertheless the scope of this route reported here to secondary molybdenum carbene compounds should be extended to other transition metals, and this possibility is under active investigation.

Experimental Section

General Data. All manipulations were performed under argon atmosphere by using standard Schlenk techniques or in a BS531 Jacomex drybox filled with nitrogen. Solvents were dried, distilled, and deaerated before use. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were distilled from sodium benzophenone ketyl immediately before use; CH_2Cl_2 was distilled first from P_2O_5 and then from Na_2CO_3. All other chemicals were used as received. The cationic complexes $[MoCp^*(CO)_3L]^+$ (**2a–e**) and the molybdenum hydride **1** were prepared following the known procedure.[15] Infrared spectra were recorded on a Pye Unicam SP 1000 spectrophotometer using 0.1-mm cells with KBr windows for solution and KBr pellets for Nujol mulls and were calibrated with polystyrene film. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Brucker WP80 FT or AM 300 Wb instrument. All NMR chemical shifts, δ, are in parts per million relative to Me_4Si for ^1H NMR, CD_2Cl_2 (δ 53.8 ppm) or $CD_3C_6H_5$ (δ 21.3 ppm) for ^{13}C, and 85% H_3PO_4 for ^{31}P signals. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon.

1. Preparation of $MoCp^*(CO)_3CHO$ (3a). To 0.050 g (0.15 mmol) of $[MoCp^*(CO)_4]^+PF_6^-$ (**2a**) in 1 mL of methanol was added 0.019 g (0.5 mmol) of $NaBH_4$ at −80 °C. The resulting suspension was stirred and slowly warmed to −30 °C. Around −70 °C the starting material was dissolved and the reaction occurred immediately. Complex **3a** was precipitated by cooling again the mixture to −80 °C and the solvent removed by filtration. The resultant yellow powder was dried under vacuo at 0 °C for 5–10 min and stored at −20 °C. The ^1H NMR spectrum recorded at −80 °C ($CD_3C_6D_5$) revealed that the solid contained a small amount (5–10%) of $MoCp^*(CO)_3H$ (**1a**), the byproduct of thermal decay of **3a**, which was impossible to eliminate.

3a: IR (cm^{-1}, Nujol) 2045 (s, ν_{CO}), 1950 (s, ν_{CO}), 1650 (m, ν_{CO}); ^1H NMR (CD_2Cl_2, −80 °C) δ 14.68 (s, 1 H, CHO), 2.00 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2, −70 °C): δ 272.2 (d, $^1J_{CH}$ = 148.9 Hz, CHO), 236.2 (s, CO trans), 227.6 (s, CO cis), 107.3 (s, C_5Me_5), 10.5 (q, $^1J_{CH}$ = 128.4 Hz, C_5Me_5).

2. Preparation of $MoCp^*(CO)_2(L)CHO$ (L = $P(OPh_3)$, 3b; L = PPh_3, 3c; L = PPh_2Me, 3d; L = PMe_3, 3e). General Procedure. In a mortar 0.5 mmol of $[MoCp^*(CO)_3L]^+PF_6^-$ (**2a–e**) and 0.076 g (2 mmol) of $NaBH_4$ were carefully ground before being placed in a Schlenk tube. The solid mixture was deaerated in vacuo for 5 min before being cooled at −80 °C. Then, 3 mL of cold methanol (−80 °C) was added and the suspension stirred, slowly warmed until the reaction began, and maintained for a 30-min period. All of the solid dissolved as the reaction occurred. The reaction temperatures, which depended on the nucleophilic properties of the starting cation, are compiled in Table III. After completion, the reaction medium was cooled again to −80 °C to precipitate the formyl complex, which was isolated by filtration of the solvent at −80 °C. After recrystallization in cold ether to cleanly eliminate the methanol, the formyl compounds were isolated as spectroscopically pure samples in 90–95% yield. Complexes **3b–e** could be stored in solid state at −20 °C for several months, but their decomposition occurred in 1–5 h at room temperature, which prevented their characterization by elemental analysis. The cis/trans isomer ratio was determined from the integrated ^1H NMR spectrum ($CD_3C_6D_5$, −30 °C) and compiled in Table III.

Table III. Selectivity (Cis/Trans) Determined from the Integrated ^1H NMR Spectrum

complex	L	T, °C	cis/trans ratio
3b	$P(OPh)_3$	−30	50/50
3c	PPh_3	−50	10/90
3d	PPh_2Me	−40	30/70
3e	PMe_3	−20	95/5

3b: IR (cm^{-1}, Nujol) 1960 (s, ν_{CO}), 1890 (s, ν_{CO}), 1605 (m, ν_{CO}).

cis-**3b**: ^1H NMR ($C_6D_5CD_3$, −30 °C) δ 14.73 (d, 1 H, $^3J_{PH}$ = 5.7 Hz, CHO), 7.50 (m, 15 H, Ph), 1.69 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 276.4 (dd, $^1J_{CH}$ = 141.5 Hz, $^3J_{CP}$ = 36.2 Hz, CHO), 235.9 (s, CO), 234.7 (d, $^2J_{CP}$ = 38.0 Hz, CO), 137.5 (m, Ph), 106.4 (s, C_5Me_5), 10.7 (q, $^1J_{CH}$ = 127.3 Hz, C_5Me_5); ^{31}P NMR (CD_2Cl_2, −30 °C) δ 166.0.

trans-**3b**: ^1H NMR ($C_6D_5CD_3$, −30 °C) δ 14.64 (d, 1 H, $^3J_{PH}$ = 5.3 Hz, CHO), 7.50 (m, 15 H, Ph), 1.67 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 268.6 (dd, $^1J_{CH}$ = 151.0 Hz, $^3J_{CP}$ = 9.6 Hz, CHO), 243.6 (d, $^2J_{CP}$ = 35.5 Hz, CO), 137.5 (m, Ph), 106.1 (s, C_5Me_5), 10.5 (q, $^1J_{CH}$ = 127.3 Hz, C_5Me_5); ^{31}P NMR (CD_2Cl_2, −30 °C) δ 184.5.

3c: IR (cm^{-1}, Nujol) 1932 (s, ν_{CO}), 1862 (s, ν_{CO}), 1602 (m, ν_{CO}).

cis-**3c**: ^1H NMR ($C_6D_5CD_3$, −30 °C) δ 14.60 (d, 1 H, $^3J_{PH}$ = 5.1 Hz, CHO), 7.05 (m, 15 H, Ph), 1.70 (s, 15 H, C_5Me_5); ^{31}P NMR (CD_2Cl_2, −30 °C) δ 71.7.

trans-**3c**: ^1H NMR ($C_6D_5CD_3$, −30 °C) δ 14.28 (d, 1 H, $^3J_{PH}$ = 7.3 Hz, CHO), 7.05 (m, 15 H, Ph), 1.70 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 277.8 (dd, $^1J_{CH}$ = 144.5 Hz, $^3J_{CP}$ = 9.6 Hz, CHO), 250.4 (d, $^2J_{CP}$ = 26.0 Hz, CO), 129.0 (m, Ph), 105.0 (s, C_5Me_5), 10.7 (q, $^1J_{CH}$ = 128.0 Hz, C_5Me_5); ^{31}P NMR (CD_2Cl_2, −30 °C) δ 65.4.

3d: IR (cm^{-1}, Nujol) 1940 (s, ν_{CO}), 1862 (s, ν_{CO}), 1600 (m, ν_{CO}).

cis-**3d**: ^1H NMR ($C_6D_5CD_3$, −30 °C) δ 14.68 (d, 1 H, $^3J_{PH}$ = 4.6 Hz, CHO), 7.50 (m, 15 H, Ph), 2.09 (d, $^2J_{PH}$ = 8.7 Hz, 3 H, PMe), 1.56 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 283.6 (dd, $^1J_{CH}$ = 135.0 Hz, $^3J_{CP}$ = 25.0 Hz, CHO), 242.0 (s, CO), 249.7 (d, $^2J_{CP}$ = 26.0 Hz, CO), 132.5 (m, Ph), 105.2 (s, C_5Me_5), 18.2 (dq, $^2J_{PC}$ = 33.3 Hz, $^1J_{CH}$ = 132 Hz, PMe), 10.4 (q, $^1J_{CH}$ = 127.4 Hz, C_5Me_5); ^{31}P NMR (CD_2Cl_2, −30 °C) δ 49.5.

trans-**3d**: ^1H NMR ($C_6D_5CD_3$, −30 °C) δ 14.91 (d, 1 H, $^3J_{PH}$ = 8.4 Hz, CHO), 7.50 (m, 15 H, Ph), 2.07 (d, $^2J_{PH}$ = 8.5 Hz, 3 H, PMe), 1.46 (s, 15 H, C_5Me_5); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 273.1 (dd, $^1J_{CH}$ = 149.0 Hz, $^3J_{CP}$ = 9.6 Hz, CHO), 237.5 (d, $^2J_{CP}$ = 26.0 Hz, CO), 132.5 (m, Ph), 105.1 (s, C_5Me_5), 16.9 (dq, $^2J_{PC}$ = 29.3 Hz, $^1J_{CH}$ = 131.1 Hz, PMe), 10.1 (q, $^1J_{CH}$ = 127.5 Hz, C_5Me_5); ^{31}P NMR (CD_2Cl_2, −30 °C) δ 43.4.

3e: IR (cm^{-1}, Nujol) 1935 (s, ν_{CO}), 1890 (s, ν_{CO}), 1600 (m, ν_{CO}).

cis-**3e**: ^1H NMR ($C_6D_5CD_3$, 0 °C) δ 14.68 (d, 1 H, $^3J_{PH}$ = 1.2 Hz, CHO), 1.91 (s, 15 H, C_5Me_5), 1.34 (d, $^2J_{PH}$ = 9.0 Hz, PMe_3); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 287.1 (dd, $^1J_{CH}$ = 137.3 Hz, $^3J_{CP}$ = 27.1 Hz, CHO), 242.1 (s, CO), 249.5 (d, $^2J_{CP}$ = 29.0 Hz, CO), 105.8 (s, C_5Me_5), 17.1 (dq, $^2J_{PC}$ = 30 Hz, $^1J_{CH}$ = 127 Hz, PMe_3), 11.2 (q, $^1J_{CH}$ = 127.0 Hz, C_5Me_5); ^{31}P NMR (CD_2Cl_2, −30 °C) δ 18.8.

trans-**3e**: ^1H NMR ($C_6D_5CD_3$, 0 °C) δ 14.42 (d, 1 H, $^3J_{PH}$ = 5.1 Hz, CHO), 1.91 (s, 15 H, C_5Me_5), 1.34 (d, $^2J_{PH}$ = 8.9 Hz, 9 H, PMe_3); ^{31}P NMR (CD_2Cl_2, 0 °C) δ 22.4.

3. X-ray Crystal Structure Determination of 3e. Single crystals suitable fro single-crystal X-ray diffraction studies were grown from toluene/pentane solution at −80 °C. Since the crystals were thermally and air sensitive, they were wrapped up in an epoxy glue matrix and the data were collected at 128 K with an Enraf-Nonius CAD 4 diffractometer. Table IV gives the crystallographic data, data collection parameters, and refined details. The structure was solved with a Patterson map that revealed the

Table IV. Experimental Crystallographic Data for 3e

formula	$(MoPO_3C_{16}H_{23})_2 \cdot CH_3OH$
fw	424.33
cryst system	monoclinic
space group	$P2_1/c$
a, Å	14.530 (8)
b, Å	8.244 (12)
c, Å	15.991 (8)
β, deg	94.28 (5)
V, Å^3	1910 (2)
Z	4
d_{calcd}, g·cm^{-1}	1.475
$F(000)$	844
μ(Mo Kα), cm^{-1}	7.6 (no absorptn correctn)
T, K	128 ± 1
cryst size, mm	0.35 × 0.20 × 0.15
radiatn, Å	λ(Mo Kα) = 0.710 69 Å
max 2θ, deg	50
scan	$\omega/2\theta$ = 1
t_{max} (for one measure), s	60
std (every 3600 s)	4,1,−1; 3,0,0; 5,0,−2
variance of std	0.6% (no appreciable decay)
data collected	3402
obsd data ($I > 3\sigma(I)$)	1589
R(isotropic)	0.090
R(anisotropic)	0.062
final R	0.051
R_w	0.044
	$1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2)]^{-1/2}$
max residuals (e Å^{-3})	0.34

molybdenum. The remaining non-hydrogen atoms of the structure are found after a scale factor refinement and a Fourier difference. After isotropic (R = 0.12) refinement a solvent molecule (methanol) appears. After an anisotropic (R = 0.062) refinement of all the non-hydrogen atoms, the hydrogen atoms were located by a Fourier differences map between 0.52 and 0.34 e A^{-3}. The whole structure was refined by the full-matrix least-square techniques. Selected interatomic distances and angles are given in Table II. Final positional parameters and equivalent thermal parameters and F_o and F_c values are available as supplementary material.

4. Decomposition of MoCp*(CO)$_2$(L)CHO (3b–e). Toluene solutions (1.0 M, 0.5 mL) of formyl complexes **3b–e** were stored at 20 °C for 72 h. Solvent was removed under vacuum, and the residue was taken up in benzene-d_6 yielding a bright yellow solution. The ^{1}H NMR spectrum showed the spectroscopically quantitative conversion of the formyl complex to the hydride analogue Mo(C_5Me_5)(CO)$_2$(L)H (**1b–e**) by comparison to the authentic samples.[15,30]

A solution of 0.060 g (0.120 mmol) of **3d** in 1.2 mL of benzene-d_6 was placed in four NMR tubes. In tube 2, 0.050 g (0.270 mmol) of 9,10-dihydroanthracene was added whereas, in tube 3, 0.020 g (0.250 mmol) of trimethylphosphine was added and, in tube 4, the solution was diluted four times with solvent. Proton NMR spectra were recorded while the probe was gradually warmed. A similar behavior was observed for the four samples.

5. Monitoring the Decomposition of MoCp*(CO)$_2$(L)CHO (3c–e). Formyl compounds **3c–e** were dissolved in 0.4 mL of toluene-d_8, cooled to −80 °C. The tubes were shaken and transferred to a −80 °C NMR probe. The ^{1}H NMR spectrum are recorded between −80 °C and +36 °C, each 5 or 10 °C. Upon warming the trans formyl isomer (*trans*-**3c–e**) decomposed first in MoCp*(CO)$_3$H (**1a**) and free phosphine; whereas the cis isomers converted, at higher temperature, in the *cis*-MoCp*(CO)$_2$(L)H (**1c–e**). The reaction of MoCp*(CO)$_3$H (**1a**) and the free phosphine was also independently observed. The decomposition of **3b** occurred from −30 °C for both cis and trans isomers, which remained in the 50/50 ratio to completion. At 25 °C, a reaction between **1a** and the free ligand occurred affording *cis*-**1b**.

6. Preparation and Characterization of [MoCp*(CO)$_2$(PPh$_3$)(CHOMe)]$^+$PF$_6^-$ (4). To a Schlenk tube were introduced 0.258 g (0.5 mmol) of **3c** and 10 mL of CH_2Cl_2 cooled to −80 °C. Then 52 μL (0.5 mmol) of CH_3SO_3F was added to the yellow solution. The color immediately changed to red-orange, and after being stirred for 0.5 h at −80 °C, the reaction mixture was slowly warmed to −10 °C. At this temperature, 0.123 g (0.75 mmol) of NH_4PF_6 was added before warming to 20 °C over a 3-h period. The solvent was evaporated to dryness and the residue washed with ether and extracted with chloroform (3 × 15 mL). After concentration of the solution to 10 mL, pentane was added until the solution became cloudy and the mixture stored overnight to −20 °C. The solid was filtered, washed with pentane, and dried under vacuum. A yellow-orange microcrystalline powder was obtained (0.221 g, 60%). Spectroscopic data indicated that the solid contained a cis/trans isomer mixture in 30/70 to 10/90 ratio depending on the crystallization step.

4: IR (cm^{-1}, Nujol) 2030 (s, ν_{CO}), 1995 (m, ν_{CO}), 1935 (m, ν_{CO}), 1130 (m, ν_{OMe}), 840 (s, ν_{PF}). Anal. Calcd for $C_{32}H_{34}MoO_3P_2F_6 \cdot 0.5CH_2Cl_2$: C, 49.60; H, 4.55. Found: C, 49.82; H, 4.61.

trans-**4**: ^{1}H NMR ($CDCl_3$, 20 °C) δ 12.45 (d, 1 H, $^3J_{PH}$ = 5.5 Hz, C*H*OMe), 7.60 (m, 15 H, Ph), 4.02 (s, 3 H, OMe), 1.95 (s, 15 H, C_5Me_5); {^{1}H}^{13}C NMR ($CDCl_3$, −50 °C) δ 330.58 (d, $^2J_{PC}$ = 6.8 Hz, *C*HOMe), 227.57 (d, $^2J_{PC}$ = 30.5 Hz, CO), 131.64 (m, Ph), 118.49 (d, $^1J_{PC}$ = 87.5 Hz, C_{ipso}), 108.81 (s, C_5Me_5), 66.38 (s, OMe), 10.70 (s, C_5Me_5); {^{1}H}^{31}P NMR ($CDCl_3$, 85% H_3PO_4, −50 °C) δ 54.6 (s, PPh_3), −143.8 (sept, J_{PF} = 713 Hz, PF_6).

cis-**4**: ^{1}H NMR ($CDCl_3$, 20 °C) δ 12.52 (d, 1 H, $^3J_{PH}$ = 1.5 Hz, C*H*OMe), 7.60 (m, 15 H, Ph), 4.80 (s, 3 H, OMe), 1.96 (s, 15 H, C_5Me_5); {^{1}H}^{13}C NMR ($CDCl_3$, −50 °C) δ 339.33 (d, $^2J_{PC}$ = 25.4 Hz, *C*HOMe), 235.81 (d, $^2J_{PC}$ = 29.7 Hz, CO), 233.62 (d, $^2J_{PC}$ = 4.0 Hz, CO), 131.64 (m, Ph), 118.49 (d, $^1J_{PC}$ = 87.5 Hz, C_{ipso}), 109.37 (s, C_5Me_5), 64.94 (s, OMe), 10.66 (s, C_5Me_5); {^{1}H}^{31}P NMR ($CDCl_3$, 85% H_3PO_4, −50 °C) δ 52.8 (s, PPh_3), −143.8 (sept, J_{PF} = 713 Hz, PF_6).

7. Attempted Reaction between 3c and 4. The methoxycarbene **4** (0.25 g, 0.043 mmol) was dissolved in 0.5 mL of CD_2Cl_2 at −60 °C, and the resulting solution was transferred in a NMR tube. A NMR spectrum was recorded for checking before an excess of the formly complex **3c** (0.029 g, 0.050 mmol) was added at this temperature. Upon warming, ^{1}H NMR spectra were recorded each 10 °C. The reduction of **4** was not observed until **3c** thermally decomposed around 25 °C.

8. Reaction of 3c with Ph$_3$C$^+$PF$_6^-$. The trityl salt (0.198 g, 0.5 mmol) and 0.289 g (0.5 mmol) of **3c** were dissolved in 5 mL of CH_2Cl_2 at −80 °C. The solution was slowly warmed to 20 °C before the solvent was removed under vacuum. The solid residue, washed with ether (4 × 20 mL) to remove Ph_3CH (identified by GC), was crystallized from chloroform/ether to afford 0.288 g (75% yield) of [MoCp*(CO)$_3$(PPh$_3$)]$^+$PF$_6^-$ (**2c**), which was analyzed by IR and ^{1}H NMR spectroscopy and compared with an authentic sample.[15] A neutral compound, soluble in ether, was isolated and identified as MoCp*(CO)$_2$(PMe$_3$)CH_2OCH_3 (**8**) by comparison with an authentic sample.[15] Compound **8** was recovered in 40% yield.

9. Reaction of 3e with CH$_3$SO$_3$CF$_3$. To a CH_2Cl_2 solution of **3e** (0.196 g, 0.5 mmol) at −70 °C was added 52 μL (0.5 mmol) of CH_3SO_3F. Following the same procedure as described above (see section 6) 0.139 g of [MoCp*(CO)$_3$(PMe$_3$)]$^+$PF$_6^-$ (**2e**) was isolated (55% yield). Compound **2e** was found to be pure by ^{1}H NMR and IR by comparison with an authentic sample.[15]

10. Generation and Spectral Characterization of [MoCp*(CO)$_2$(PPh$_3$)CHOH]$^+$CF$_3$COO$^-$ (6). To a Schlenk tube containing 0.150 g (0.290 mmol) of **3c** dissolved in 0.4 mL of CD_2Cl_2 cooled at −70 °C was added 4 μL (0.59 mmol) of CF_3COOH. The yellow solution immediately turned red-orange. After being stirred 10 min, the mixture was filtered and transferred by cannula in a NMR tube. Whereas both cis and trans isomers were observed by ^{1}H NMR, only the trans one was observed by ^{13}C NMR.

6: ^{1}H NMR ($CDCl_3$, −60 °C) δ 13.20 (m, 0.1 H, C*H*OH cis), 12.99 (d, $^3J_{PH}$ = 12.6 Hz, 0.9 H, C*H*OH trans), 9.27 (br, 1 H, CHO*H*), 7.50 (m, 15 H, Ph), 1.74 (s, 15 H, C_5Me_5); ^{13}C NMR ($CDCl_3$, −60 °C) δ 307.78 (dd, $^1J_{CH}$ = 134.8 Hz, $^2J_{CP}$ = 22.0 Hz, CHOH), 244.80 (d, $^2J_{PC}$ = 27.0 Hz, CO), 131.0 (m, Ph), 155.23 (q, $^1J_{CF}$ = 287.0 Hz, CF_3), 106.18 (s, C_5Me_5), 10.23 (s, C_5Me_5).

11. Synthesis and Characterization of [MoCp*(CO)$_2$(PPh$_2$Me)(CHOSiMe$_3$)]$^+$SO$_3$CF$_3$ (7). To a yellow CH_2Cl_2 solution (5 mL) of **3d** (0.320 g, 0.6 mmol) cooled to 0 °C was added 120 μL of $Me_3SiOSO_2CF_3$ (0.74 mmol) under stirring. The color changed to red-orange, and after the solution was warmed to 20 °C, 30 mL of pentane was added to precipitate 0.348 g of **7** as an oily red spectroscopically pure sample. **7** decomposed slowly at room temperature over around 24 h but was indefinitely stable

at -20 °C. The cis/trans ratio calculated from integrated ^1H 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: ^1H 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_5Me_5), 18.0 (d, $^2J_{PC}$ = 32.0 Hz, PMe), 10.87 (s, C_5Me_5), 1.02 (s, Si*Me*$_3$); ^{31}P NMR (CD_2Cl_2, -60 °C) δ 37.09 (s, PPh_2Me).

cis-7: ^1H 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_5Me_5), 19.8 (d, $^2J_{PC}$ = 31.8 Hz, PMe), 10.87 (s, C_5Me_5), 2.16 (s, Si*Me*$_3$); ^{31}P NMR (CD_2Cl_2, -60 °C) δ 54.50 (s, PPh_2Me).

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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

(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