if this results from hindered rotation about the Al–C bond or because of hindered rotation about the O–C bond of the bridging group. In all cases there was no evidence for dissociation of the Al–O–Al bridge bond in solution. Further, in separate experiments, it was shown that THF did not form a stable adduct with **1a** nor did diethyl ether form a stable adduct with **2a**.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. **1a**, 136763-63-8; **1b**, 136763-64-9; **1c**, 136763-65-0; **2a**, 136763-66-1; **2b**, 136763-67-2; **2c**, 136763-68-3; Me_3Al, 75-24-1; Et_3Al, 97-93-8; $(i\text{-}Bu)_3Al$, 100-99-2; *l*-menthol, 2216-51-5; *l*-borneol, 464-45-9.

Supplementary Material Available: Complete listings of bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates, and isotropic thermal parameters and unit cell packing diagrams for **1a,c** and **2a** (17 pages); listings of observed and calculated structure factors for **1a,c** and **2a** (67 pages). Ordering information is given on any current masthead page.

Coordination Chemistry of Group 14 Metalloles. 7.[1] Fluxional Behavior of *cis*-MLL′(η^4-metallole)$_2$ (M = Mo, W) Complexes

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Complexes of the type *cis*-MLL′(n^4-metallole)$_2$ exhibit fluxionality in solution. A study by variable-temperature ^1H, ^{13}C, and ^{31}P NMR allows the determination of factors which govern fluxionality and the mechanisms which explain isomerization. When L = L′ = CO, an equilibrium between rotational enantiomers (cis-Δ uu and cis-Λ uu) is observed; in addition, when the metallole is C-unsubstituted or substituted by methyl groups in the 3- and 4-positions, a rotational racemic diastereoisomer is also observed. The interconversion between diastereoisomers is faster than the one between enantiomers for steric reasons. For L = L′ = PMe_3 or for L = CO and L′ = $P(OPh)_3$ (ligands which have, respectively, the same electronic effect but are more sterically demanding than two CO ligands), only an equilibrium between cis-Δ uu and cis-Λ uu enantiomers is present. When the metalloles are phenyl C-substituted, diastereoisomers cannot be detected. These interconversions are well explained by a ring rotation mechanism. A different situation occurs when L and L′ are complementary ligands [L = CO; L′ = PPh_3, PPh_2Me, P(*p*-tol)$_3$]; then the coexistence of cis-Δ uu and trans-ou is observed. The different isomers are detected, namely, by the different coupling constants of the carbonyl signals with the phosphorus nucleus. This equilibrium implies the coexistence of a fast ring rotation mechanism (cis-Δ uu $\rightleftharpoons$ cis-Λ uu interconversion) and a slow Bailar twist (cis-Δ uu $\rightleftharpoons$ trans-ou interconversion).

Introduction

We previously described the crystal structure and the dynamic stereochemistry of complexes of the type LL′-bis(η^4-metallole)transition metal[2–4] (L = CO, L′ = PPh_3). The X-ray study of dicarbonylbis(η^4-1,1,3,4-tetramethylsilole)molybdenum (**7**) (Chart I) revealed that the structure is cis-uu[5] (Chart II). The structures of other related complexes were assumed to be identical by analogy.

In solution, the situation is different, since the IR spectra of these complexes showed the presence of diastereoisomers for all the series. [These isomers are rotamers; however, the terms diastereoisomers and enantiomers are used for more clarity.] Their fluxional behavior was investigated by variable-temperature NMR experiments. Dicarbonyl complexes showed an averaged ^1H NMR spectrum at 300 K, but at ~100 K the nonequivalence of the olefinic and of the methyl protons in the 3- and 4-positions was observed (as predicted by the X-ray analysis). Nevertheless, diastereoisomers were not observed with this technique.

The ^1H NMR spectrum of carbonylbis(η^4-1,1-dimethylsilole)(triphenylphosphine)molybdenum (**1**) showed four signals for the olefinic protons at 300 K. This is consistent with a fluxional cis complex which isomerizes via a ring rotation mechanism (Figure 1). But, in contrast to that of the dicarbonyl complexes, its low-temperature spectrum showed 12 signals for the olefinic protons and 8 for the methyl ones. This was attributed to a slow equilibrium between the cis-uu and the trans-ou diastereoisomers; indeed, the coexistence of one cis isomer and the trans-ou one was the only one compatible with such multiplicity. This interconversion was explained via an intramolecular nondissociative process; a Bailar twist[8] was invoked as being the most consistent with the η^4-coordi-

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[1] Part 6: Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Butll. Soc. Catalana Cienc.*, in press.

[2] Carré, F.; Colomer, E.; Corriu, R. J. P.; Lheureux, M.; Cavé, A. *J. Organomet. Chem.* **1987**, *331*, 29.

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[5] For nomenclature rules, see refs 6 and 7.

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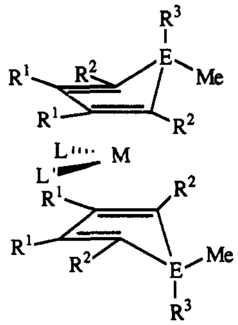
Chart I. List of the Compounds Studied in This Work



no.	M	E	R^1	R^2	R^3	L	L'
1	Mo	Si	H	H	Me	CO	PPh$_3$
2	Mo	Si	H	H	Me	CO	CO
3	Mo	Si	H	H	Me	CO	PPh$_2$Me
4	Mo	Si	H	H	Me	CO	P(OPh)$_3$
5	Mo	Si	H	H	Me	CO	P(p-tolyl)$_3$
6	Mo	Si	H	H	Me	PMe$_3$	PMe$_3$
7	Mo	Si	Me	H	Me	CO	CO
8	Mo	Si	Me	H	Ph	CO	CO
9	W	Si	Me	H	PhCH$_2$	CO	CO
10	W	Si	Me	H	Me	CO	CO
11	Mo	Si	H	Ph	Fp	CO	CO
12	W	Si	H	Ph	Fp	CO	CO
13	Mo	Ge	Me	H	Me	CO	CO

Fp = Fe(CO)$_2$(η^5-C$_5$H$_5$)

nation of the diene ligands.[2] Signals corresponding to two diastereosisomers were also observed by variable-temperature ^{31}P NMR studies. Nevertheless, other features (observation of only one signal for each endo- and exomethyl proton at 300 K and double irradiation experiments at 173 K, which showed that each signal corresponding to the olefinic protons was associated with another one) can only be explained by the presence of a ring rotation mechanism[7] in each diastereoisomer (Figure 1).

Some important points were, however, obscure:

(i) The observation of two pairs of signals for the olefinic protons in 1 was not consistent with the coexistence of a Bailar twist and a ring rotation mechanism. Indeed, for the olefinic protons β to silicon (the same reasoning applies to the α ones) the e and f populations will have E, F, I, and J chemical environments, and g and h, G, H, I, and J, respectively (Figure 1). At high temperature this should result in one averaged signal.

Since the Bailar twist was invoked on the basis of the multiplicity of the signals in the low-temperature ^{1}H NMR spectrum of 1, some doubt remains on whether some signals were masked. If this were the case, an equilibrium between two cis diastereoisomers (bearing 16 signals for the olefinic protons and also 8 for the methyl ones) could explain the experimental facts and be rationalized by a ring rotation exclusively. (The equilibrium between cis-ΔΛ uu and trans-ou isomers should result in 6 + 6 signals for the olefinic protons instead of 8 + 8 for two cis isomers).

(ii) In the case of the dicarbonyl complexes **2**, **7–10**, and **13**, the presence of diastereoisomers could only be detected by IR spectroscopy. Variable-temperature ^{1}H NMR measurements revealed the nonequivalence of signals as predicted for the cis-uu geometry, whereas no information could be obtained from ^{13}C NMR spectroscopy. It was then difficult to rationalize why the trans isomer was not detected by these techniques, contrary to complex 1.

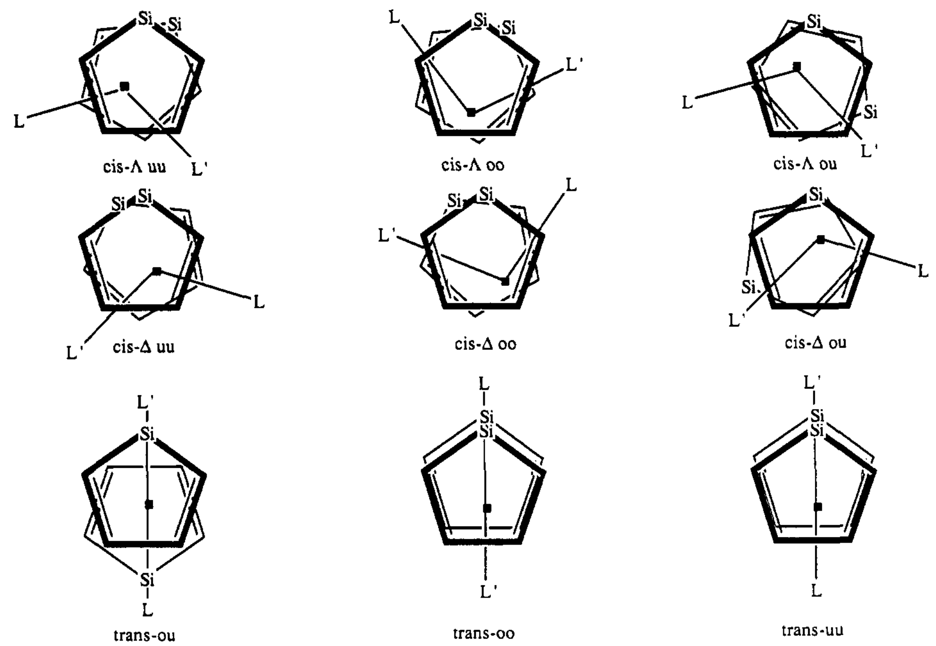
This situation prompted us to find new nonequivocal evidence for the presence of the trans isomer for complex 1 and give also a reasonable explanation for the behavior of the *cis*-dicarbonyl complexes.

Experimental Section

New compounds were prepared under nitrogen using a vacuum line and Schlenk tubes. UV irradiations were performed in a quartz vessel using a 450-W Hanovia lamp except for the preparation of complex **6**.

NMR spectra were recorded under nitrogen with a Varian EM 390, a Bruker AW 80, a Bruker WP 200 SY, or a Bruker WM 360

Chart II. Possible Isomers for MLL'(η^4-metallole)$_2$ Complexes



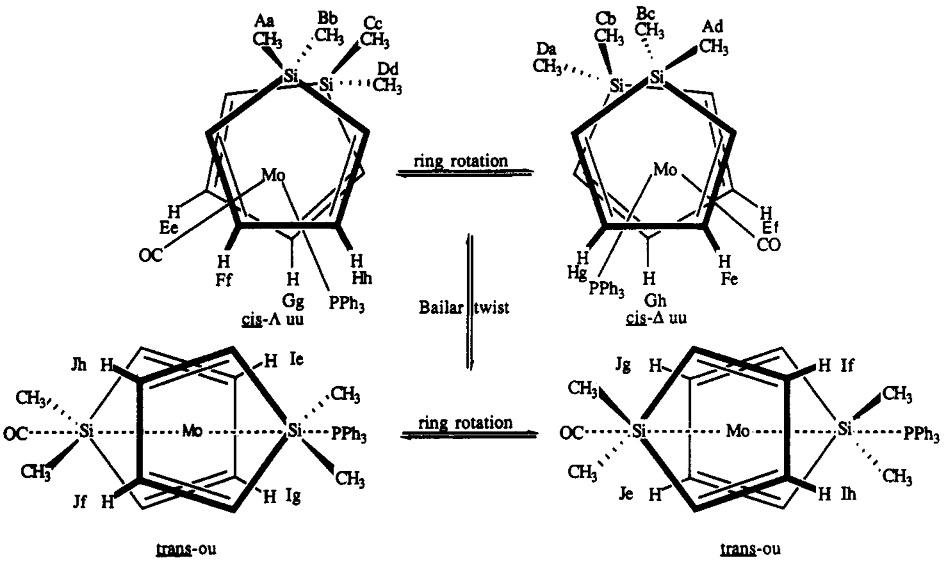


Figure 1. Ring rotation is faster than the twist and explains the racemization cis-Λ uu ⇌ cis-Δ uu. This mechanism also plays a role in the trans-ou isomer. Capital letters refer to chemical shifts and lower case letters to populations.

WB instrument (chemical shifts are relative to Me_4Si, internal, or H_3PO_4, external, unless stated otherwise).

Activation energies at the coalescence temperature were calculated using Eyring's equation.[9]

Variable-Temperature ^1H NMR Spectra of Complex 1. NMR: at 300 K (360 MHz) in toluene-d_8, δ 5.42, 4.61, 2.15, and 1.69 (broad singlets, olefinic); at 360 K, δ 5.42 (m), 4.61 (m), 2.15 (dd), and 1.69 (d). Irradiation of the different signals led to the following modifications. Irradiation at δ 5.42: δ 4.61 (d, J = 6.6 Hz), 2.15 (s), and 1.69 (dd, J = 6.6 and 2.5 Hz). Irradiation at δ 4.61: δ 5.42 (t, J = 6.3 Hz), 2.15 (dd, J = 6.3 and 2.5 Hz), and 1.69 (s). Irradiation at δ 2.15: all other signals were multiplets. Irradiation at δ 1.69: δ 5.42 (td, J = 6.3 and 2.5 Hz), 4.61 (s), and 2.15 (d, J = 6.3 Hz).

^1H NMR at 403 K (90 MHz) in p-dichlorobenzene (the olefinic protons β to Si are obscured by the solvent) (chemical shifts are given using the signal of exo-CH_3 as reference): δ 2.10 and 1.50 (broad s, olefinic α to Si) and 0.60 (s, endo-CH_3). Irradiation of the signal at δ 2.10 leads to the disappearance of the one at δ 1.50 and vice versa.

Low-temperature ^1H NMR spectral data were given in ref 2.

Variable-Temperature ^{13}C NMR Spectra of Complex 1. The sample was studied at 90.5 MHz in CD_2Cl_2 NMR at 300 K (δ): 241.1 (d, $J_{C,P}$ = 14 Hz, CO); 137–127 (aromatic); 81.1 and 68.3 (olefinic, β to Si); 45.2 and 25.8 (olefinic, α to Si); 11.4 (endo-CH_3) and −0.4 (exo-CH_3). NMR at 173 K (δ): 243.8 ($J_{P,C}$ = 17 Hz, trans CO) and 237.4 ($J_{P,C}$ = 9 Hz, cis CO); 104.0, 95.1, 88.2, 85.3, 81.9, 77.2, 72.3, 67.3, 65.5, 50.7, 44.4, and 36.3 (olefinic); 30.8, 25.0, 14.8, 11.1, 9.7, −1.2, −3.3, and −5.2 (CH_3) (attributions α and β to Si and endo and exo are difficult to assign). T_{coal} = 200 K; ΔG^*_{coal} = 37 kJ mol^{-1}.

Carbonylbis(η^4-1,1-dimethylsilole)(methyldiphenylphosphine)molybdenum (3). A solution of 2[10] (748 mg, 2 mmol) and methyldiphenylphosphine (400 mg, 2 mmol) in 200 mL of benzene was irradiated for 10 h. The reaction was monitored by IR spectroscopy, and after this time, a strong band had appeared at 1886 cm^{-1}. The solvent was pumped off, the residue was dissolved in hexane, and the mixture was filtered through a fritted funnel (G 4). The filtrate was kept at −20 °C and afforded 230 mg of 3 (21%): yellow crystals, mp 117–118 °C, ν_{CO} (hexane) 1902 (shoulder) and 1890 (s) cm^{-1}; mass spectrum m/e (assignment) 517 (M^+ − CO − H for ^{98}Mo), 345 (M^+ − PPh_2Me − H), 318 (M^+ − PPh_2Me − CO). Anal. Calcd for $C_{26}H_{33}MoOPSi_2$: C, 57.35; H, 6.07. Found: C, 57.61; H, 6.07. ^1H NMR at 80 MHz (C_6D_6) and 300 K (δ): 7.13 and 7.02 (m, 10 H, aromatic); 4.83 (m, 4 H, olefinic, β to Si); 1.68 and 1.52 (m, olefinic, α to Si); 1.63 (d, $J_{P,H}$ = 9 Hz, P–CH_3) (these three signals integrate to 7 H); 0.56 (s, 6 H, endo-CH_3) and 0.08 (s, 6 H, exo-CH_3). ^1H NMR at 360 MHz (CD_2Cl_2) and 273 K (δ): 7.35 and 7.23 (m, aromatic); 4.88 and 4.75 (broad s, olefinic, β to Si); 2.02 (d, $J_{P,H}$ = 9 Hz, P–CH_3); 1.68 and 1.32 (broad s, olefinic, α to Si); 1.46 (s, endo-CH_3) and −0.13 (s, exo-CH_3). ^1H NMR at 173 K (δ): (all signals are broad singlets) 7.68, 7.40, 7.25, and 6.92 (aromatic); 6.05, 5.87, 5.42, 5.17, 4.94, 4.60, 3.30, 2.99, 2.90, 2.58, 1.55, and 1.18 (olefinic, the attributions α and β to Si are difficult to establish for minor signals); 2.12 and 1.97 (P–CH_3); 0.79, 0.63, 0.52, and 0.30 (endo-CH_3); −0.03, −0.17, −0.27, and −0.33 (exo-CH_3). ^{13}C NMR at 90.5 MHz (CD_2Cl_2) and 273 K (δ): 242.9 (d, $J_{P,C}$ = 15 Hz, CO); 137.2 (d, $J_{P,C}$ = 36 Hz, aromatic, ipso); 131.7, 129.6, and 128.1 (aromatic); 91.4 and 83.4 (olefinic β to Si); 48.8 and 44.6 (olefinic, α to Si); 18.0 (d, $J_{P,C}$ = 31 Hz, P–CH_3); 11.6 (endo-CH_3) and 0.2 (exo-CH_3). ^{13}C NMR at 173 K (δ): 244.2 (peak width at half-height 27 Hz, CO); 243.3 (peak width at half-height 40 Hz, CO); 139.9 (d, $J_{P,C}$ = 40 Hz) and 133.0 (d, $J_{P,C}$ = 34 Hz) (aromatic, ipso, diastereotopic); 136.2, 130.8–126.9 (aromatic); 106.1, 89.7, 80.2, and 80.0 (olefinic, β to Si); 57.8, 49.7, 38.1, and 36.0 (olefinic, α to Si); 17.6 (d, $J_{P,C}$ ~ 25 Hz) and 16.5 (d, $J_{P,C}$ = 30 Hz) (P–CH_3); 12.4–11.1 (endo-CH_3) and 0.7–0.5 (exo-CH_3). Other minor signals are observed in the olefinic range, but it is difficult to attribute them to the compound or to impurities. For P–CH_3 the coalescence temperature is T_{coal} = 189 K, and ΔG^*_{coal} = 36.9 kJ mol^{-1}. ^{31}P NMR at 81.0 MHz (CD_2Cl_2) (δ): 273 K, 47.1; 173 K, 47.8 and 46.6 (relative intensities 1:6). T_{coal} = 187 K; ΔG^*_{coal} = 36.7 kJ mol^{-1}.

Carbonylbis(η^4-1,1-dimethylsilole)(triphenyl phosphite)molybdenum (4). A solution of complex 2[10] (744 mg, 2 mmol) and triphenyl phosphite (620 mg, 2 mmol) in 200 mL of benzene was irradiated with UV light and the reaction monitored by IR spectroscopy until the ν_{CO} band at ~1985 cm^{-1} disappeared (~10 h). The solvent was then pumped off and the oily residue dissolved in hexane and chromatographed on a Florisil column (Merck) with hexane; the yellow band was collected, concentrated to ~5 mL, and kept at −78 °C to afford 525 mg of 4 (40%): yellow crystals, mp 124–125 °C; ν_{CO} (hexane) 1938 cm^{-1}; mass spectrum m/e (assignment) 628 (M^+ − CO for ^{98}Mo). Anal. Calcd for $C_{31}H_{35}MoO_4PSi_2$: C, 56.88; H, 5.36. Found: C, 57.15; H, 5.85. ^1H NMR at 80 MHz (C_6D_6) and 300 K (δ): 7.14–6.80 (m, 15 H, aromatic); 5.81 and 4.49 (m, 4 H, olefinic, β to Si); 2.04–1.70 (m, 4 H, olefinic, α to Si); 0.18 (s, 6 H, endo-CH_3) and −0.04 (s, 6 H, exo-CH_3). ^1H NMR at 360 MHz (CD_2Cl_2) and 283 K (δ): 7.40 and 7.20 (m, 15 H, aromatic); 5.79 (t, J = 6 Hz, 2 H, olefinic, β to Si); 4.28 (broad s, 2 H, olefinic, β to Si); 1.91 (d, J = 5.5 Hz, 2 H, olefinic, α to Si); 1.57 (t, J = 6 Hz, 2 H, olefinic, α to Si); 0.16 (s, 6 H, endo-CH_3) and −0.14 (s, 6 H, exo-CH_3). ^1H NMR at 183 K (δ): 7.40 and 7.20 (m, aromatic); 5.89, 5.58, 4.94, and 2.89 (broad s, olefinic, β to Si); 2.23 and 1.31 (broad s, olefinic,

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(10) Burns, G. T.; Colomer, E.; Corriu, R. J. P.; Lheureux, M.; Dubac, J.; Laporterie, A.; Iloughmane, H. *Organometallics* 1987, *6*, 1398.

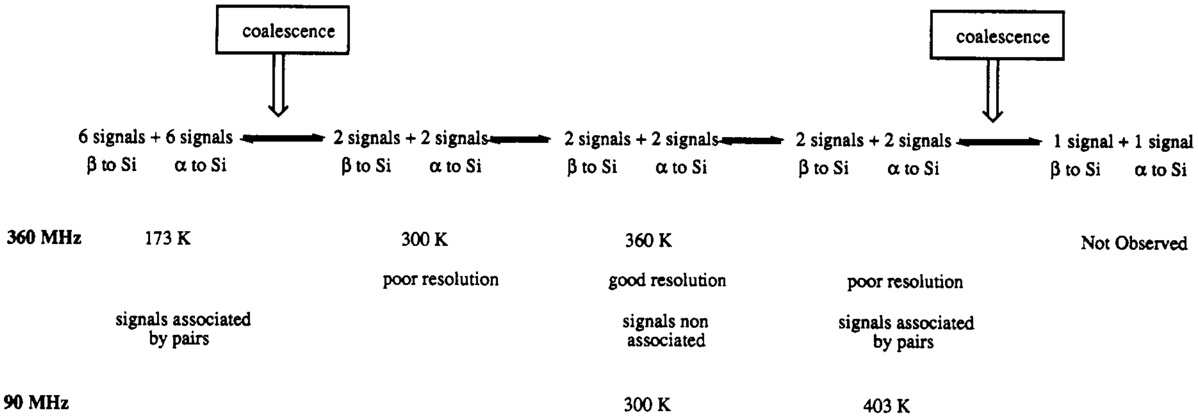


Figure 2. Schematic representation of the ^{1}H NMR spectra of the olefinic protons in complex **1** at different fields and temperatures.

α to Si); 1.48 (broad s, olefinic α to Si), 0.03 (s, endo-CH_3), and −0.23 (s, exo-CH_3) (signals at 1.48, 0.03, and −0.23 do not decoalesce at this temperature). ^{13}C NMR at 90.5 MHz (CD_2Cl_2) and 283 K (δ): 234.4 (d, $J_{P,C}$ = 19.8 Hz, CO); 151.9 (d, $J_{P,C}$ = 9 Hz, aromatic, ipso); 129.9 and 124.7 (aromatic, meta and para); 121.3 (d, $J_{P,C}$ = 4.5 Hz, aromatic, ortho); 82.7 and 77.1 (olefinic, β to Si); 50.0 and 46.8 (olefinic, α to Si); 11.5 (endo-CH_3) and −1.3 (exo-CH_3). ^{13}C NMR at 183 K (δ): 233.7 (d, $J_{P,C}$ = 19 Hz, CO); 151.9 (d, $J_{P,C}$ = 9 Hz, aromatic, ipso); 129.9, 124.7, and 121.3 (aromatic); 88.1, 83.6, 75.3, and 73.4 (olefinic, β to Si); 50.7, 48.1, and 41.5 (olefinic, α to Si); 10.3 and 9.5 (endo-CH_3) and −2.8 and −3.9 (exo-CH_3) (the signal at δ 48.1 does not decoalesce at this temperature). T_{coal} = 188 K for exo- and endo-CH_3; ΔG^*_{coal} = 38.5 kJ mol^{-1}. ^{31}P NMR at 81.0 MHz (CD_2Cl_2) (δ): 273 K, −6.0; 183 K, −9.2.

Attempted Preparation of Carbonylbis(η^4-1,1-dimethylsilole)(tri-*p*-tolylphosphine)molybdenum (5). A solution of 2[10] (900 mg, 2.4 mmol) and P(p-tol)$_3$ (731 mg, 2.4 mmol) in 500 mL of toluene was irradiated with UV light. The reaction was monitored by IR spectroscopy, and after 20 h, two new carbonyl bands were observed at 1900 and 1886 cm^{-1}. The solvent was pumped off, and residue was extracted with hexane, and the mixture was filtered through a frit (G 4). Standing at −18 or at −78 °C did not lead to the formation of crystals. Attempts of purification by column chromatography (Florisil, silica gel, alumina) led to decomposition.

The compound was studied without purification; it appeared as a gum after evaporation of the solvent. It showed two ν_{CO} bands corresponding to unreacted **2** and two new ones attributed to **5** at 1901 and 1887 cm^{-1}. Mass spectrum of the mixture: *m/e* (assignment) 650 (M$^+$ for ^{98}Mo), 635 (M$^+$ − CH_3), 346 (M$^+$ − P(p-tol)$_3$).

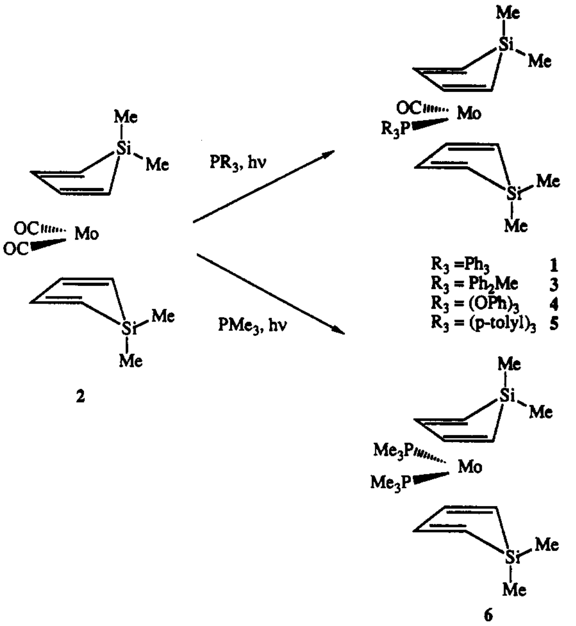
^{13}C NMR at 90.5 MHz (CD_2Cl_2) and 273 K (δ): 241.5 (d, $J_{P,C}$ = 14 Hz, CO). ^{13}C NMR at 183 K (δ): 244.3 (d, $J_{P,C}$ = 20 Hz, trans-CO) and 238.0 (d, $J_{P,C}$ = 10 Hz, cis-CO). T_{coal} = 200 K; ΔG^*_{coal} = 37.9 kJ mol^{-1}. Other signals are difficult to attribute, since the sample is not pure. ^{31}P NMR at 81.0 MHz (CD_2Cl_2) and 293 K (δ): 65.4 (major, attributed to **5** by comparison to the chemical shift of **1**, (70 ppm), 47.9 (minor), and −7.3 (minor attributed to the free phosphine). ^{31}P NMR at 183 K (δ): 69.5 and 62.8 (in a ratio 7:5). T_{coal} = 208 K; ΔG^*_{coal} = 38.0 kJ mol^{-1}. (This signal is the only one that exhibits decoalescence.)

Bis(η^4-1,1-dimethylsilole)bis(trimethylphosphine)molybdenum (6). A solution of complex 2[10] (372 mg, 1 mmol) and trimethylphosphine (0.5 mL, excess) in 150 mL of benzene was irradiated with a 100-W medium-pressure Hanovia lamp in a quartz vessel. The reaction was monitored by IR spectroscopy, and after 1.5 h, the ν_{CO} absorption due to **2** had disappeared. The solvent was pumped off, and the residue was crystallized from hexane at −20 °C to afford 170 mg of orange crystals of **6** (yield 36%): mp 181–182 °C; mass spectrum *m/e* (assignment) 394 (M$^+$ − PMe_3 for ^{98}Mo). Anal. Calcd for $C_{18}H_{38}MoP_2Si_2$: C, 46.15; H, 8.12. Found: C, 46.96; H, 8.30 (a more satisfactory result could not be obtained).

Variable-Temperature ^{1}H NMR Spectra of 9.[1] NMR at 360 MHz (CD_2Cl_2) and 273 K (δ): 7.23 (t, J = 8 Hz, 4 H, *m*-H aromatic); 7.00 (t, J = 8 Hz, 2 H, *p*-H aromatic); 6.89 (d, J = 8 Hz, 4 H, *o*-H aromatic); 2.02 (s, 12 H, C–CH_3); 1.77 (s, 4 H, CH_2); 1.32 (s, 4 H, olefinic) and 0.38 (s, 6 H, endo-CH_3). NMR at 163 K (δ): 7.23, 7.00, and 6.89 (aromatic); 2.09 and 1.74 (C–CH_3); 1.78 (CH_2 and olefinic); 0.81 (olefinic) and 0.39 (endo-CH_3). T_{coal} = 176 K for CH_3–C; ΔG^*_{coal} = 34.0 kJ mol^{-1}.

Results and Discussion

UV irradiation of **2** in the presence of trimethylphosphine leads to the substitution of both carbonyl ligands and formation of **6** (eq 1). It is interesting to note that monosubstitution cannot be obtained, in contrast to the action of PPh_3, PPh_2Me, P(p-tol)$_3$, and P(OPh)$_3$, probably due to steric rather than electronic effects.[11] Carbonyl ligands cannot be substituted in other complexes by PPh_3, and when complex **7** is treated by PMe_3, the silole ligands are displaced instead, giving a mixture of carbonyl(phosphine)molybdenum complexes. This is also, likely, due to a steric interaction with the substituents in the ring (methyl groups in 3,4- or phenyl groups in 2,5-positions).



(1)

The ^{1}H NMR spectrum of complex **1** at 173 K (360 MHz) consists of six signals for each type of olefinic proton, double-irradiation experiments showed that these signals are associated by pairs.[2] At 300 K the olefinic protons appear as four broad singlets, and at 360 K these signals become well-resolved multiplets. Using a lower field spectrometer (90 MHz), the signals are already well re-

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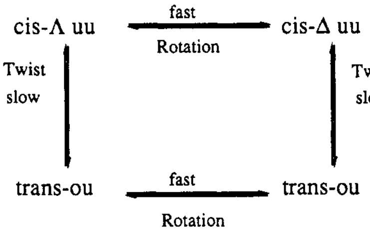
Table I. NMR Data for *cis*-Mo(η^4-1,1-Me$_2$silole)$_2$(PMe$_3$)$_2$ (6) in Toluene-d_8

	^{1}H NMR (360 MHz): δ, ppm					^{13}C NMR (50.32 MHz): δ, ppm					^{31}P NMR (81.02 MHz):
T, K	β =CH	α =CH	PMe$_3$	endo-Me	exo-Me	β =C	α =C	PMe$_3$	endo-Me	exo-Me	δ, ppm
343	4.62 (s)	1.22 (s)	0.76 (d)[a]	0.66	0.39	87.9	40.7	~20[b]	14.0	1.9	
300						96.9, 79.6	46.3, 33.9	~20[b]	14.0	1.9	18.2
263	5.40, 4.01	1.87, −0.37	1.16 (d)[a]	0.34	−0.10[c]						
193											19.3

[a] $J_{H,P}$ = 5 Hz. [b] Masked by toluene. [c] In CD$_2$Cl$_2$.

Scheme I. Mechanism for the Isomerization of MLL′(η^4-metallole)$_2$ (L = CO, L′ = PPh$_3$) via Ring Rotation and Bailar Twist[a]



[a] A ring rotation takes place in isomer trans-ou as shown by the equivalence of protons.

solved at 300 K, but at a higher temperature (403 K) they appear again as broad singlets and can be associated by double-irradiation experiments. Figure 2 gives a schematic representation of the experimental findings.

These observations are consistent with the coexistence of a Bailar twist and a ring rotation mechanism (Scheme I). At 173 K both mechanisms are slow compared to the shift differences[12] but the ring rotation is fast with respect to the proton relaxation time (this allows us to make a distinction between them). With an increase of the temperature, coalescence of the different signals occurs giving an averaged spectrum which is well resolved at higher temperature (360 K, 360 MHz) or at a lower field (300 K, 90 MHz). However, double-irradiation experiments show that the twist is still slow with respect to the proton relaxation time. At 403 K (90 MHz), the signals are poorly resolved announcing another coalescence and the twist becomes fast with respect to the proton relaxation time. This new coalescence cannot be observed due to temperature limitations.

The ^{13}C NMR spectrum of 1 at 300 K shows, in addition to the signals corresponding to the methyl, olefinic, and aromatic carbon nuclei, one signal at 241.1 ppm corresponding to CO with a $J_{P,C}$ = 14 Hz. At 173 K the signal has decoalesced and given rise to two signals at 243.8 ($J_{P,C}$ = 17 Hz) and 237.4 ppm ($J_{P,C}$ = 9 Hz). These values fall in the range of trans and cis coupling constants between carbonyls and phosphines in octahedral complexes of molybdenum and tungsten.[13,14] The free energy of activation at the coalescence temperature is ΔG^*_{coal} = 37 kJ mol^{-1}; this value is the same as that obtained from ^{31}P NMR[2] spectroscopy, and it shows that both coalescences correspond to the same phenomenon. This observation constitutes a direct proof for the existence of both cis and trans isomers.

Complex 3 shows a close behavior to that of 1 in both ^{1}H and ^{13}C NMR spectroscopy. Unfortunately, the signals for the CO nuclei are not well resolved at low temperature and the coupling constants cannot be determined; however, their peak widths at half-height are different, and this might be attributed to different couplings with the phosphorus nucleus. Two signals due to CH$_3$–P are also observed at low temperature and correspond to the different isomers. The presence of diastereoisomers is also shown by ^{31}P NMR spectroscopy. ΔG^*_{coal} can be calculated and has the same value whatever the observed nucleus, carbon or phosphorus. In IR spectroscopy, two ν_{CO} bands are also present in solution. Independently of diastereoisomerism, chirality at molybdenum is shown by the diastereotopy of the aromatic ipso carbon nuclei, which appear as two distinct signals at 139.9 and 133 ppm.

Table II. ^{1}H Variable-Temperature NMR Spectra of Complexes 7–13 in CD$_2$Cl$_2$ or CD$_2$Cl$_2$/CS$_2$

complex	T, K	δ(=CH), ppm	T_c, K	$\Delta G^*(T_c)$, kJ mol^{-1}	ref
7	300	1.71	183	34	2
	168	2.12, 1.19			
8	300	1.96	193	36	2
	173	2.38, 1.36			
9	300	1.32	183	34	this work
	163	1.78, 0.81			
10	300	1.44	178	33	2
	168	1.74, 0.92			
11[a]	300	5.10	178	34	10
	163	5.30, 4.64			
12[a]	300	4.90	205	38	10
	163	5.13, 4.40			
13[a]	300	2.02	208	38	2
	183	2.42, 1.39			

[a] CD$_2$Cl$_2$/CS$_2$ solvent.

Table III. Δν Values, Coalescence Temperatures, and Activation Energies for *cis*-Mo(η^4-1,1-dimethylsilole)$_2$(PMe$_3$)$_2$ (6)

obsd nucleus	Δν, Hz	T_c, K	$\Delta G^*(T_c)$, kJ mol^{-1}
β =CH	500	325	60.5
α =CH	804	325	59.0
β =C	871	323	58.9
α =C	625	323	59.7

Complex 5 cannot be obtained in a pure state. However, in its IR and ^{13}C and ^{31}P NMR spectra it exhibits very close behavior to that of 1 and 3. Complex 4, in which the monohapto ligands are CO and P(OPh)$_3$, behaves quite differently. Only one carbonyl absorption band is observed in the IR spectrum at 1938 cm^{-1}, contrary to other complexes, indicating that only one diastereoisomer is present in solution. The ^{1}H and ^{13}C NMR studies are consistent with the equilibrium between cis-Λ uu and cis-Δ uu enantiomers; in particular only one signal is observed for the CO resonance ($J_{P,C}$ = 19–20 Hz) whatever the temperature. This large coupling is the normal value observed in cis complexes with phosphite ligands.[13,14] The absence of isomers is also confirmed by ^{31}P NMR spectroscopy, since only one signal is observed whatever the temperature.

Complex 6 is particularly interesting, since at 300 K (studied at 90 or 360 MHz) the olefinic protons are close to coalescence. At 343 K (360 MHz) a well-resolved spectrum is obtained (Table I). At lower temperature (263

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Table IV. ν_{CO} **Absorption Bands for Complexes 2–5 and 7–13 in Hexane**

complex	ν_{CO}, cm^{-1}	ref
1	1916, 1890	2
2[a]	2000 (sh), 1990, 1955 (sh), 1940	2
3	1902 (sh), 1890	this work
4	1938	this work
5	1901, 1887	this work
7	1978, 1972, 1919, 1912	2, 10
8	1975, 1972, 1918, 1912	1, 2
9	1982, 1976, 1922, 1915	1
10	1976, 1970, 1917, 1908	2, 10
11[b]	1988 (br), 1973 (br), 1933 (br)	4
12[b]	1988 (br), 1973 (br), 1932 (br)	4
13	1970, 1963, 1912, 1905	2, 10

[a] sh = shoulder; br = broad. In cyclohexane. [b] In toluene.

K) two signals are observed for each type of olefinic protons (a situation close to that of the dicarbonyl complexes **7**–**13** but at a much higher temperature) (Table II). The signals can be associated by double-irradiation experiments. The same features are observed for **6** in ^{13}C NMR spectroscopy, contrary to previous observations with complexes **2**, **7**, **8**, **10**, and **13**.[2]

From these studies the activation energy at the coalescence temperature can be calculated (Table III) using Eyring's equation.[9] It is interesting to compare the high value obtained ($\Delta G^*_{coal} \sim 60$ kJ mol^{-1}) to those obtained for the dicarbonyl complexes ($\sim$35 kJ mol^{-1}), and this suggests that the motion is slowed down by steric hindrance. Indeed, complex **2**, without substituents at carbon atoms, shows only a broadening of the olefinic protons at 163 K (360 MHz) and decoalescence is not attained.

Variable-temperature ^{31}P NMR measurements on **6** show only one signal in the interval 300–193 K. This is in contrast with the observation of two signals for ^{31}P in complexes **1**, **3**, and **5** and suggests that the trans isomer is not present.

A detailed study of the IR spectra of complexes **7**–**10** and **13** (Table IV, Figure 3) indicates that the four bands can be associated according to their intensity and the spectra appear then as the superimposition of those of two compounds. The more intense bands (also the less intense ones) are separated by $\sim$60 cm^{-1}, and this suggests that both isomers possess the same structure. Indeed, it is difficult to rationalize why a cis and a trans arrangement of the carbonyl ligands would give so similar patterns; on the contrary, two cis isomers should give very similar ν_{CO} absorption bands. These carbonyl absorptions are to be compared to those of *cis*-dicarbonylbis(η^4-diene)molybdenum and -tungsten complexes studied by Kreiter and Ozkar.[15] For complex **2** only shoulders are observed; for complexes **11** and **12** the resolution is lower than 10 cm^{-1} and superimposition of the ν_{CO} bands due to the Fe(CO)$_2$(η^5-C$_5$H$_5$) moiety occurs, avoiding the observation of the four bands due to Mo(CO)$_2$, if present.

Conclusion

Complexes **1**, **3**, and **5** exist in solution as an equilibrium mixture of cis-ΔΛ uu and trans-ou isomers. The only possibility to rationalize this interconversion, without bond cleavage, is a molecular motion,[16–18] and among the known ones, a Bailar twist[8] is the more consistent with the η^4-coordination of the dienic ligands[2] rather than a Springer–Sievers[19] or a Rây-Dutt twist.[20] Ligand rotation takes also place and is faster than the twist.

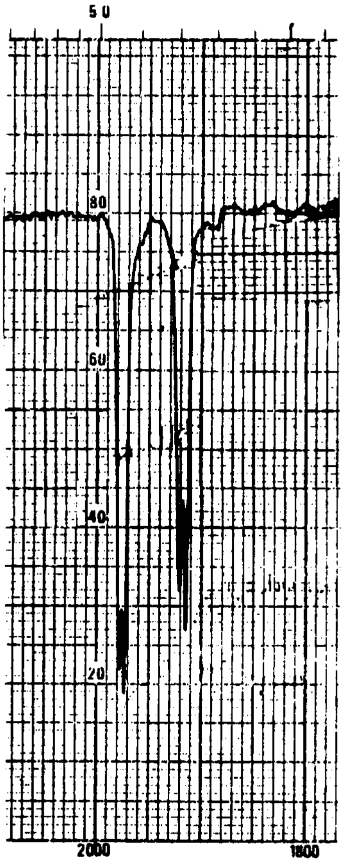

Figure 3. Carbonyl absorption bands of *cis*-dicarbonyl(η^4-metallole)$_2$metal complexes. Spectrum given for *cis*-dicarbonyl(η^4-1,1,3,4-tetramethylsilole)molybdenum.

IR spectroscopy is less time dependent than NMR spectroscopy and provides an instantaneous picture of the situation: coexistence of cis and trans isomers. Low-temperature NMR spectroscopy shows the signals corresponding to both isomers, meaning that both motions are slow compared to the shift difference, but spin-saturation-transfer experiments on the proton show that the twist is slow, and the ring rotation fast, with respect to the proton relaxation time (T_1).[2]

Complexes **2**, **7**–**10**, and **13**, on the contrary, undergo isomerization between two cis isomers, via a ring rotation. It is difficult to determine which isomers are present: cis-ΔΛ uu can be assumed on the basis of the structure determined in the crystal,[2] but the other isomer can be both cis-ΔΛ ou or cis-ΔΛ oo (Chart II).

This difference in behavior can be easily understood, since CO and phosphines are complementary ligands[21] (in other terms, CO is a good electron acceptor whereas phosphines are good electron donors) and they will easily adopt a trans disposition. For complexes with two identical monohapto ligands (the electronic effects of which are in competition) the trans isomer will not be favored.

From IR and NMR evidence, complex **4** is not present as a mixture of diastereoisomers. This can be explained by the following: (i) The electronic nature of phosphites is such that they are, contrary to phosphines, good electron acceptors. For this reason the monohapto ligands will

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Scheme II. Mechanism for the Isomerization of $ML_2(\eta^4\text{-metallole})_2$ Complexes (L = CO, PMe_3) via Ring Rotation[a]

$$\begin{tikzcd}
\text{cis-}\Lambda\text{ uu} \arrow[r, "\text{fast}"] \arrow[d, dash, "\text{slow}"'] & \text{cis-}\Lambda\text{ ou} \arrow[d, dash, "\text{slow}"] \\
\text{cis-}\Delta\text{ uu} \arrow[r, "\text{fast}"] & \text{cis-}\Delta\text{ ou}
\end{tikzcd}$$

[a] Isomer cis-ΔΛ oo could be present instead of cis-ΔΛ ou.

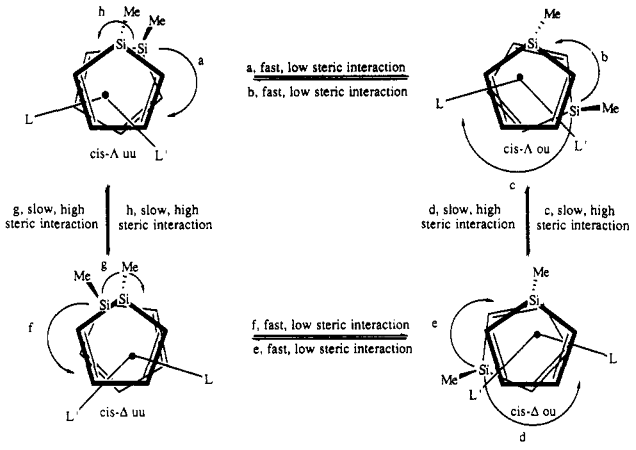
adopt a cis disposition. (ii) The steric crowding of the bulky phosphite will not favor a cis-ou or a cis-oo isomer because the interaction between the ligand and the endo-methyl group.

The study of the spectra of complex **6** is more difficult, since IR spectroscopy cannot help in this case. However, ^1H, ^{13}C, and ^{31}P NMR spectroscopy do not give any evidence for the presence of diastereoisomers. The monohapto ligands, which are identical, will adopt a cis geometry, and although Me_3P is not very bulky, the presence of two ligands might not allow isomers cis-ou or cis-oo as is the case for **4**.

The proposed explanation is that, for complexes with two identical, nonsterically demanding, monohapto ligands, two cis isomers coexist in rapid equilibrium, as a virtual single isomer, in slow equilibrium with their enantiomers (also observed as a virtual single isomer) (Scheme II). In complexes **11** and **12**, the presence of diastereoisomers cannot be detected. A doubt remains about their presence, since the ν_{CO} absorption bands are broad; however, we may assume that, due to steric hindrance of the phenyl groups, only the equilibrium between cis-Δ uu and cis-Λ uu isomers, observed by ^1H NMR[4] spectroscopy, is present. On the other hand, for complex **1** (with CO and PPh_3) the situation is different and the twist mechanism becomes significant (the gain in stability due to the trans arrangement of the monohapto ligands is the driving force) (Scheme I).

It is difficult, however, to understand why the equilibrium between diastereoisomers is faster than the one between enantiomers for dicarbonyl complexes **2**, **7–10**, and **13**. The proposed explanation is that the conversion between cis-Λ uu and cis-Δ uu may be slowed down by the interaction between the endo-methyls, as the one between cis-Λ uu and cis-Λ ou is less sterically demanding (Scheme III). Indeed, the conversion between enantiomers should occur via ring rotations following paths c, d, g, and h; steric interactions between the endo-methyl groups or one endo-methyl and the monohapto ligands might slow down the motion. On the contrary, isomerizations between diastereoisomers, through paths a, b, e, and f are free of steric hindrance.

Scheme III. Isomerization of the Dicarbonyl Complexes by a Ring Rotation Mechanism



The dynamics of quasi-octahedral (η^4-diene)metal complexes has been extensively studied by Kreiter and coworkers,[6,7,15,22] who demonstrated their fluxionality. However, the presence of the metallole ring, instead of dienes, brings some important differences that can be attributed to the presence of the ERR′ (E = Si, Ge) group. Thus, the former have the uu conformation, since the latter possess the oo one,[2] and the trans isomers are not significant in the case of the diene complexes. It is interesting to note that twisting mechanisms play an important role in number of chelate complexes but had never been invoked to explain the fluxional behavior of diene complexes.

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