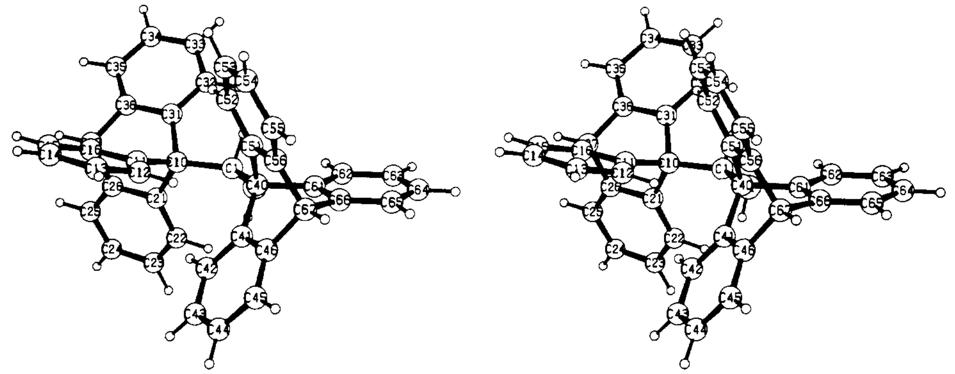


Figure 3. Stereoview of the X-ray structure of bis(9-triptycyl)carbinol (Tp_2CHOH).

of two and only two residual diastereomers is fully consistent with this analysis. Configurational assignments were made on the basis of the appearance of the aromatic $^{13}C\{^1H\}$ NMR region, which featured 18 signals for **1b** but only 12 for **1a**,[14] and by an analysis of the aromatic ^1H NMR region, which featured two ABCD spin systems for **1b** but only one for **1a**. Accordingly, **1a** was identified as the residual meso isomer and **1b** as the residual DL pair.[15]

That gear slippage is slow on the laboratory time scale is established by the isolation of two diastereomers of **1** at ambient temperature. This is also consistent with the extraordinarily large central C–C–C bond angle of 129° in a closely related compound, bis(9-triptycyl)carbinol (Tp_2CHOH, Figure 3):[16-20] the magnitude of the angle deformation indicates that the molecule is under considerable internal strain, with the Tp groups tightly meshed, and implies that gear slippage, which would require further expansion of the central bond angle, should be a highly unfavorable process. Indeed, interconversion of the diastereomers becomes readily observable only at elevated temperatures. In nitrobenzene-d_5, thermal equilibrium is attained within several hours at 156 °C; the equilibrium constant, $K(\mathbf{1b}/\mathbf{1a}) = 1.8 \pm 0.1$, corresponds to an almost statistical ratio of DL and meso isomers. The diastereomerization barriers, $\Delta G^\ddagger = 34.1$ and 33.6 kcal mol^{-1} at 156 °C,[23] are significantly higher than the topomerization barrier of ca. 20 kcal mol^{-1} calculated[1] for Tp_2CH_2, as might be expected considering that diastereomerization of **1a** or **1b** forces at least one of the two 2-methyl groups into the overcrowded central region of the transition state.[24,25]

Acknowledgments. We thank the National Science Foundation (CHE-8009670) for support of this work, Mary Baum for valuable technical assistance, and the Consiglio Nazionale delle Ricerche for a fellowship to one of us (F.C).

Supplementary Material Available: Structure factors, final positional and thermal parameters, bond lengths, bond angles, and selected torsion angles, with standard deviations, for Tp_2CHOH (28 pages). Ordering information is given on any current masthead page.

---

[13] If the gearing barrier is less than RT kcal mol^{-1},[3] a distinction between the three conformers within each of the three sets may become meaningless: Eliel, E. L. *Isr. J. Chem.* **1977**, *15*, 7.

[14] Meso isomer (**1a**): $^{13}C\{^1H\}$ NMR (25.2 MHz, $CDCl_3$) δ 147.2, 146.4, 144.3, 143.7, 132.6, 131.7, 126.8, 125.0, 124.7, 124.6, 124.2, and 123.2 (aromatic carbons); 54.8, 54.7, 25.7, 19.4, and 19.2 (aliphatic carbons). DL isomer (**1b**): δ 147.3, 146.5, 146.5, 146.1, 144.8, 144.3, 132.9, 132.0, 125.7, 125.6, 125.0, 124.9, 124.9, 124.7, 124.3, 124.0, 123.2, and 123.1 (aromatic carbons); 54.8, 54.7, 25.7, 19.7, and 19.3 (aliphatic carbons).

[15] A permutational analysis[1] reveals that two residual diastereomers are expected under the operation of any one of six different stereoisomerization modes. However, all but two of these are immediately excluded on the basis of the NMR signal multiplicity. Of the remaining two modes, one corresponds to the gearing motion depicted in Figures 1 and 2 and the other to the corresponding antigearing motion, in which rotation of the moieties is con-instead of disrotatory. Although empirical force-field calculations indicate that gearing is overwhelmingly the preferred mode,[1] the isolation of two residual diastereomers does not *by itself* rigorously exclude antigearing.[1]

[16] Crystals of Tp_2CHOH, prepared as previously described[1] and grown by slow evaporation of a pentane/ether solution, are monoclinic, space group $P2_1/n$. There are two independent molecules, primed and unprimed, of the carbinol in the unit cell. The crystals also contain 9% pentane and 6% ether solvent by NMR. The primed molecule represents a disordered arrangement of two molecules in almost the same orientation; we therefore place greater reliance in the geometry of the unprimed molecule, which is shown in Figure 3. The carbinol crystallizes as rods elongated along the b direction. Crystallographic data for Tp_2CHOH: $a = 21.385$ (5), $b = 17.408$ (6), $c = 17.433$ (5) Å; $\beta = 104.87$ (2)°, and $d_{calcd} = 1.137$ g cm^{-3} for $Z = 8$ ($C_{41}H_{28}O$, $M = 536.67$; solvent excluded from density); $R = 0.068$, $R_w = 0.076$ for 4969 reflections with $I > 2.5\sigma(I)$. Intensity data were measured on a Hilger–Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). Reflections were measured for $\theta < 48°$. The structure was solved by a multiple solution procedure [Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368]. The final refinement was carried out by block-diagonal least squares in which the matrix was partitioned into two blocks. Anisotropic thermal parameters were used for the nonhydrogen atoms of the unprimed and primed molecules, and isotropic temperature factors were used for the disordered oxygen atom, two solvent atoms, and the hydrogen atoms. The C10–C1–C40 angle assumes a value of 128.9 (3)° and 129.1 (4)° in the unprimed and primed molecule, respectively.

[17] It is noteworthy that this molecule undergoes enantiomerization exclusively through chiral structures under the constraint of gear meshing.[1]

[18] This value is comparable to the central bond angle (125–128°, as determined by electron diffraction) in di-*tert*-butylmethane.[19] We find a value of 123 Hz for the methylene ^{13}C–^1H NMR coupling constant in Tp_2CH_2, which is comparable in magnitude to the value of 125 Hz reported[19] for the methylene coupling constant in di-*tert*-butylmethane.

[19] Bartell, L. S.; Bradford, W. F. *J. Mol. Struct.* **1977**, *37*, 113.

[20] The observation of greatly expanded central bond angles in bis(triphenylmethyl) ether[21] and sulfide[22] suggests that Tp_2Se[5] and Tp_2O[2] may also have extraordinarily large central C–X–C angles, i.e., that the described phenomenon may not be unique to Tp_2X (as compared to $(trityl)_2X$) systems.

[21] Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 696.

[22] Jeffrey, G. A.; Robbins, A. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1820.

[23] The ratio of **1a** and **1b** was determined from the relative peak areas of the upfield methyl proton signals at 1.77 and 1.93 ppm (Table I) and was monitored as a function of time. The cited values of $\Delta G^\ddagger$ were obtained from a kinetic treatment[8b] of these data.

[24] We assume that the transition state for gear slippage in Tp_2CH_2 is approximated by the gear-clashed conformation **1B** in ref 1.

[25] By the same token, the barrier to interconversion of D- and L-**1b** is expected to be relatively low.

Bis(4-chloro-1-triptycyl) Ether. Separation of a Pair of Phase Isomers of Labeled Bevel Gears[1]

Yuzo Kawada and Hiizu Iwamura*

Division of Applied Molecular Science
Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

Received September 25, 1980

The idea of geared rotation has often been adopted to explain unexpectedly fast internal rotation in apparently congested molecules, e.g., hexamethylbenzene,[2] 1,1,1-tri-*tert*-butyl compounds,[3] and Ar_3Z systems.[4] Coupled rotation of two parts of

---

[1] Part 2 of this series. For part 1, see: Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547.

[2] Iroff, L. D. *J. Comput. Chem.* **1980**, *1*, 76 and references cited therein.

0002-7863/81/1503-958$01.25/0

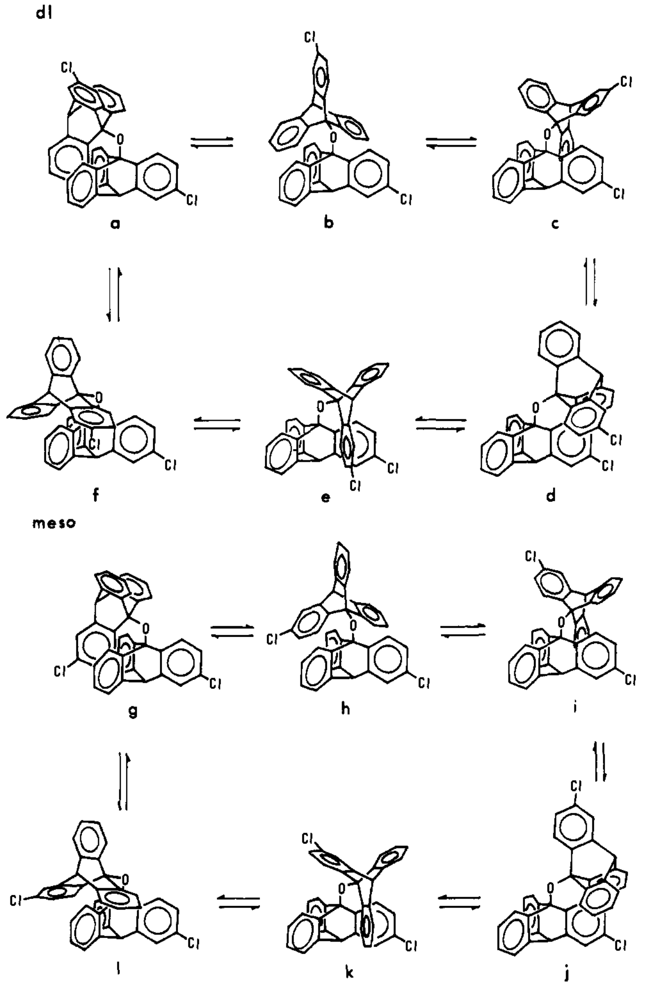


Figure 1. Phase isomers *dl* and meso of bis(4-chloro-1-triptycyl) ether (**6**). They do not interconvert unless rotation around the C–O bonds gets out of gear.

a molecule may become energetically more feasible than independent rotation of a single group. As one of the most conspicuous examples of conformational mobility of overcrowded molecules, we recently described bis(1-triptycyl) ether (**1**) in which six benzene rings were equivalent and no sign of restricted rotation around the two C–O bonds was shown by variable-temperature ^{1}H and ^{13}C NMR spectra even down to −94 °C.[1,5] Geared rotation in a literal sense about the aforementioned bonds was considered to be responsible for the high mobility.

Now, if the correlated rotation is so favorable and precise that the bevel gears do not "slip" in **1**, there is a possibility of producing a pair of "phase" isomers out of the bevel gears when one of the cogs on each wheel is labeled. They are perspectively shown for the case of the 4-chloro derivative in Figure 1.[5] In one isomer, the labeled cogs can bite each other once in a full cycle of rotation, while in the other they are one phase apart and never come next to each other. The former contains three doubly degenerate conformers: a = b, c = f, and d = e. They are all chiral, and therefore this isomer should consist of a *dl* pair. The other isomer contains a doubly generate conformer (g = j) with a plane of symmetry and a *dl* pair of conformers both doubly degenerated (h = i and k = l) and therefore should be achiral. We tentatively call this isomer meso.[6] The two isomers represent a conceptually new isomerism in the sense that there is rapid rotation around both single bonds, but it is intimately coupled to give separate isomers.

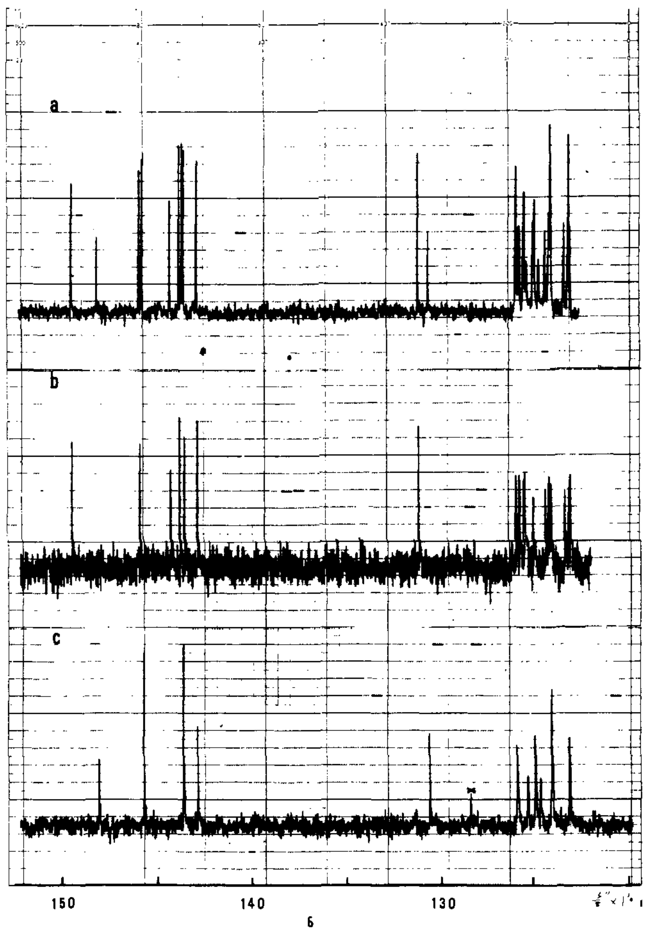


Figure 2. 25.14-MHz ^{13}C{^{1}H} NMR spectra of **6** (aromatic regions only).[11] (a) The sample before fractionation, (b) *dl* isomer, and (c) meso isomer.

In order to ascertain the possibility experimentally and to rule out the possibility of a noncorrelated pathway in the rotation of **1**, we have undertaken the synthesis and separation of a labeled derivative of **1**. As a label on the bevel gear, we chose a chloro substituent at the 4 position, because it is too far from the site of the gear biting to have any effect on the rate of the correlated rotation,[7] and yet its polar nature may become a clue to separation.[8] The synthetic route is essentially the same one as in the parent ether,[1] as is outlined in Scheme I.[9] 1-Bromo-4-chlorotriptycene (**2**) and its 1-lithio compound served as common starting materials. After being converted to the 1-carbonyl chloride **4** on the one hand and to the lithium salt of the 1-hydroperoxide on the other, they were coupled to give peroxy ester **5**. Thermolysis

---

(3) (a) Hounshell, W. D.; Iroff, L. D.; Wroczynski, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 5212. (b) Wroczynski, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1979** *101*, 3980.

(4) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

(5) By assuming the chemical shift difference of 1–3 ppm, we found the barrier height to be not higher than ca. 8 kcal mol^{-1}. A preliminary molecular mechanical calculation did not reveal any appreciable barrier. If this is taken seriously, the staggered forms as given in Figure 1 do not necessarily represent the energy minimum conformers.

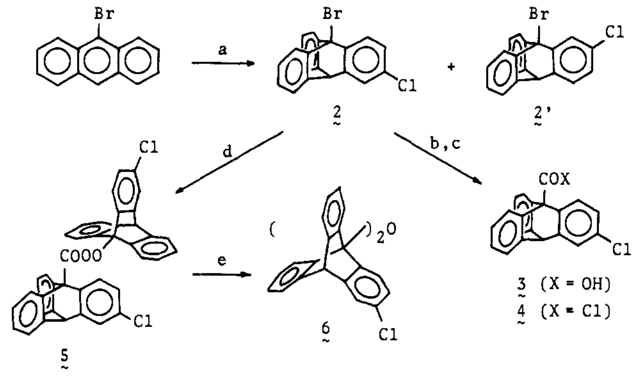
(6) This tentative nomenclature will not cover the whole range of the isomerism. For example, when all benzene rings in each triptycene moiety are identifiable, six *dl* or one meso and five *dl* isomers will result depending on symmetry.

(7) A substituent at the 2 and/or 3 position of some bulk will slow down the coupled rotation, and the resultant stereoisomerism could be too complex. To the contrary, a 4 and/or 5 substituent appears to have almost no effect on the rotation, according to molecular models.

(8) We also prepared the 5,5′-dimethyl derivative of **1** which showed no sign of separation under similar conditions.

(9) All new compounds exhibited spectral properties (IR and NMR) consistent with their structure and gave satisfactory elemental analyses. 1-Bromo-4-chloro- and 1-bromo-3-chlorotriptycenes obtained roughly in an equal amount were separated by fractional crystallization and GPC.[10] Their structures were unequivocally assigned by comparison of ^{1}H NMR. **2** (CDCl$_3$): δ 5.39 (s, 1 H), 6.9–7.2 (m, 5 H), 7.2–7.5 (t + d, 2 H + 1 H), 7.7–7.9 (dt, 3 H). **2′** (CDCl$_3$): δ 5.36 (s, 1 H), 6.9–7.2 (m, 5 H), 7.3–7.5 (dt, 3 H), 7.6–7.9 (t + d, 2 H + 1 H).

Scheme I[a]



[a] (a) 1 equiv of 2-amino-4-chlorobenzoic acid (in DME) and 1.5 equiv of isoamyl nitrite (in CH_2Cl_2) are added to the bromoanthracene (in CH_2Cl_2) under reflux, 2 h. (b) To get **3**, 1.5 equiv of *n*-butyllithium (1.6 M in hexane) is added to **2** (in C_6H_6/Et_2O = 1/2), -40 °C, 30 min, then CO_2 gas, -40 °C, 10 min. (c) To get **4**, **3** (in $CHCl_3$) is added to a refluxing $SOCl_2$ (large excess), reflux, 1 h. (d) The triptycyllithium prepared as in (b) is added to Et_2O saturated with O_2, -78 °C, 1 h, followed by addition of 0.3 equiv of **4** (in C_6H_6), room temperature, overnight. (e) In perfluorodecalin, 130-150 °C, 1 h.

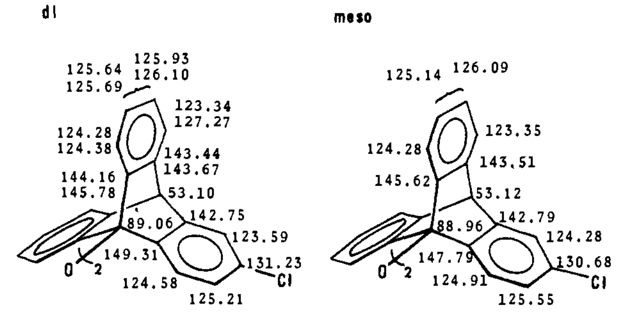


Figure 3. ^{13}C NMR chemical-shift values (ppm downfield from internal Me_4Si) in $CDCl_3$.

of **5** at 130–150 °C in perfluorodecalin gave in good yield ether **6**.

The ^{13}C spectrum (in $CDCl_3$) of **6** purified by GPC[10] and free from fractionation, whose aromatic region is reproduced in Figure 2a, exhibited more or less closely spaced doublets or triplets for most carbons in intensity ratios of 2:1 or 1:1:1,[11] indicating the presence of the *dl* and meso isomers in 2:1 ratio as expected statistically.[12] Our attempt to separate the two isomers was encouraged by the observation that a pair of signals separated by less than 1 Hz did not coalesce even at 150 °C in $CDCl_2/CDCl_2$. By applying the Eyring equation, the activation free energy for interconversion was estimated to be greater than 24.5 kcal mol^{-1}.

Separation of the isomers was finally effected by high-performance LC.[13] The ^{13}C spectra of pure isomers, *dl* (mp 397 °C) and meso (mp 383 °C),[14] are reproduced in Figure 2, parts b and c, respectively. Assignments, when possible, based on selective decoupling and comparison with model compounds, are summarized in Figure 3. Out of 12 possible aromatic carbons, 11 were separately observed for the meso isomer. The equivalence of the four unsubstituted benzene rings as well as of the two chloro-substituted rings show a rapid interconversion among the conformers.[5,15] Eighteen separate carbon signals were obtained for the *dl* isomer. The presence of a pair of carbon signals for each position in the unsubstituted benzene rings shows that the two benzene rings on each triptycene moiety are mutually diastereotopic (see Figure 1).

In conclusion, this work shows that correlated rotation is not only a theoretical concept or a phenomenon derivable from sophisticated analyses but an actual event which does not fail at ambient temperatures in this system. As a necessary corollary of the successful separation of the phase isomers, this work also provides experimental support for a high-potential-energy barrier to inversion at the dicoordinated oxygen atom.[16] If bending of the oxygen valence angle were easily attained, this mode of deformation should have led to a loose gear, and no isomers could have been obtained.

Further separation of the *dl* isomer into the optical antipodes is in progress.

---

(10) Gel permeation chromatography on JAIGEL 1H and 2H using an instrument LC-08 of Japan Analytical Industry Co. Ltd.

(11) These ratios were obtained under the FT NMR conditions which employed 16K data points for 800 Hz and warranted reliable separation and intensity of each signal. See text for the reason of 1:1:1 ratio.

(12) As the two isomers do not interconvert mutually at the reaction temperature, this ratio is a kinetically controlled value and reasonably explained by almost no effects of the 4 substituent on the sequence of homolysis, decarboxylation, and recombination of the peroxy ester **5** (see Scheme I).

(13) On a $^3/_8$ in. × 1 ft μPorasil column using hexane/benzene (8:2) with a flow rate of 2.5 mL/min.

(14) Measured by differential scanning calorimetry on a Du Pont 990 thermal analyzer. The extrapolated onset temperature of the endothermic curve obtained with a scanning rate of 5 °C/min was taken as the melting point. High-performance LC analyses of the melts revealed some mutual interconversion of both isomers. Gear slip, inversion at the oxygen atom, and homolysis-recombination are some of the possibilities for the isomerization. Kinetic and mechanistic studies are in progress.

(15) ^{13}C chemical-shift differences between the meso and *dl* isomers are small and sometimes much smaller than those caused by dissymmetry in the unlabeled benzene rings in the latter isomer. This may be ascribed to a more or less even population of possible conformers a–l.

(16) Gordon, A. J.; Gallagher, J. P. *Tetrahedron Lett.* **1970**, 2541.

Synthesis and Structure of *trans*-[[[*cis*-Tetracarbonylbis(*N*-((2-diphenylphosphinamido)ethyl)salicylaldimino-*P*)]molybdenum(0)]-*N*,*N'*,*O*,*O'*]nickel(II), a Novel Bimetal Trans-Ligating Tetradentate Schiff Base Complex with a "Fly-over" Chain Containing a Metal Atom

Charles S. Kraihanzel*

Department of Chemistry,
Lehigh University, Bethlehem, Pennsylvania 18015

Ekk Sinn

Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Gary M. Gray

J. T. Baker Chemical Co.
Phillipsburg, New Jersey 08865

Received July 18, 1980

A continuation of our studies on the reactions of coordinated phosphorus donor ligands has led to a group of novel heteronuclear bimetal complexes.[1,2] The general reaction scheme (Scheme I) leading to these complexes and the molecular structure (Figure 1) of *trans*-[*cis*-$(CO)_4Mo[PPh_2NHCH_2CH_2N{=}CH(o\text{-}C_6H_4O)]_2$]Ni (III) are shown below.[3-5] The air-stable, dark-

---

(1) Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1980**, *187*, 51.

(2) Kraihanzel, C. S.; Gray, G. M., 13th Middle Atlantic Regional Meeting of the American Chemical Society, West Long Branch, NJ, March 20–23, 1979; American Chemical Society: Washington, DC 1979; Paper IN 26.

(3) ***cis*-[Tetracarbonylbis(*N*-((2-diphenylphosphinamido)ethyl)salicylaldimine-*P*)]molybdenum(0)** (I). Salicylaldehyde (0.43 mL) was added at room temperature to a well-stirred solution of 1.39 g of *cis*-$(CO)_4Mo(PPh_2NHCH_2CH_2NH_2)_2$ in 20 mL of tetrahydrofuran. After 10 min the solvent was removed under vacuum to leave a yellow oil which recrystallized from CH_2Cl_2/hexane as a CH_2Cl_2 solvate. Heating this solid at 60° (1 mm) for 2.5 h yielded 1.5 g (94%) of CH_2Cl_2-free, analytically pure, yellow product, mp 139–140 °C. Anal. Calcd for $C_{46}H_{42}MoN_4O_6P_2$: C, 61.07; H, 4.68. Found: C, 60.88; H, 4.70.