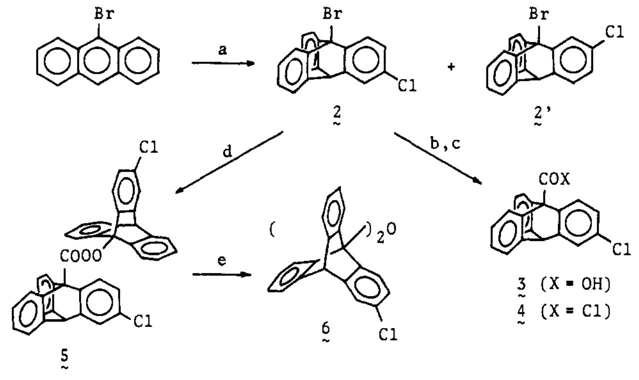
Scheme I[a]



[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.

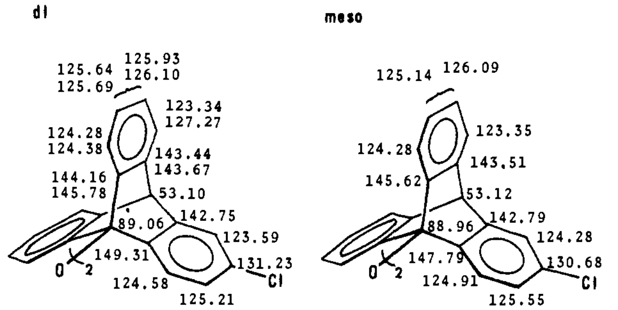


**Figure 3.** $^{13}C$ NMR chemical-shift values (ppm downfield from internal $Me_4Si$) in $CDCl_3$.

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.

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[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.

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## 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

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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-

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[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.

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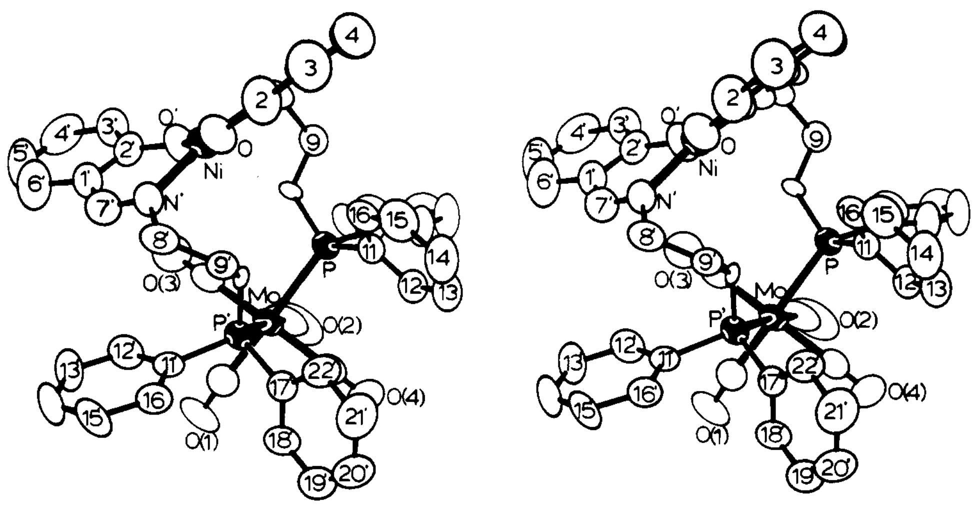
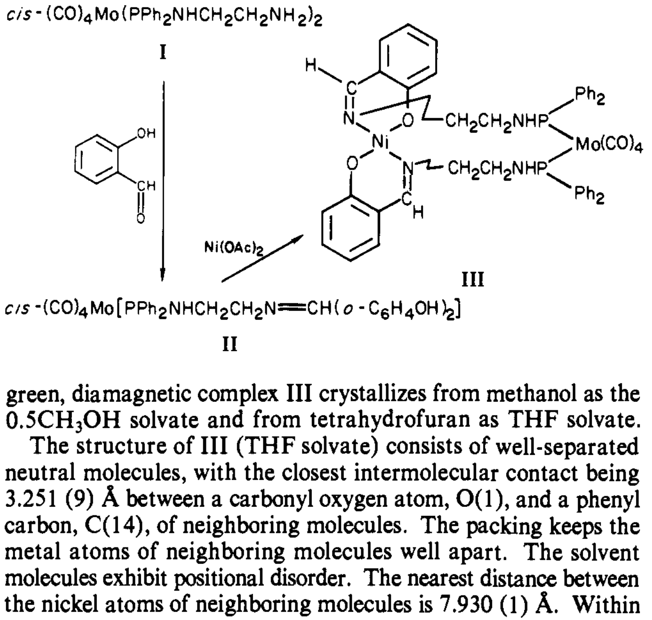


**Figure 1.** ORTEP drawing of III (stereoscopic). Positions of hydrogen atoms are not indicated.

Scheme I



green, diamagnetic complex III crystallizes from methanol as the $0.5CH_3OH$ solvate and from tetrahydrofuran as THF solvate.

The structure of III (THF solvate) consists of well-separated neutral molecules, with the closest intermolecular contact being 3.251 (9) Å between a carbonyl oxygen atom, O(1), and a phenyl carbon, C(14), of neighboring molecules. The packing keeps the metal atoms of neighboring molecules well apart. The solvent molecules exhibit positional disorder. The nearest distance between the nickel atoms of neighboring molecules is 7.930 (1) Å. Within each molecule, the $PNH(CH_2)_2N$ linkage separates the nickel(II) and molybdenum(0) atoms by 5.679 (1) Å.

The ligand environment about the molybdenum atom is a distorted octahedron with the three equatorial planes of four donor atoms meeting at angles of 89.9, 88.9, and 89.9°. The phosphorus donor atoms are bonded cis to each other, subtending an angle of 92.34 (7)° at the metal atom. The Mo–P bond lengths are 2.550 (6), 2.529 (6) Å. The carbonyl ligands trans to the P donors are more closely bonded to the metal (Mo–C = 1.976 (10) and 1.980 (10) Å) than the two carbonyl groups trans to each other (Mo–C = 1.986 (10) and 2.036 (10) Å).

The nickel(II) ion is in an approximate planar ligand geometry with a slight tetrahedral distortion. The dihedral angle ($\phi$) between the two NiNO ligand planes is 12.6°. Values of 0 and 90° for $\phi$ are necessary though not sufficient conditions for true planar and tetrahedral geometries, respectively. The tetrahedral distortion is insufficient to make the complex paramagnetic. Instead, the geometry is close to that expected for diamagnetic bis-bidentate nickel(II) salicylaldimine complexes. Beyond the $NiO_2N_2$ coordination sphere, the salicylaldimine ligands themselves show considerable distortion.

The structure of III, and by inference the structures of the divalent cobalt, iron, copper, and zinc Schiff base analogues,[2] is of interest for diverse reasons. Tetradentate Schiff base ligands derived from salicylaldehyde and short-chain primary diamines form cis square-planar complexes with nickel(II).[7] More recent reports have shown long-chain primary diamines to form trans square-planar tetradentate Schiff base complexes described as having "fly-over" chains.[8,9] These complexes and a variety of iron and cobalt complexes of "capped" porphyrins and simpler Schiff base ligands are under active study as myoglobin and hemoglobin biomimetric models for dioxygen uptake.[10–14] Inasmuch as complex I can be considered a long-chain diamine, the observed structure of III is reasonable and bears a resemblance to the previously reported structures of capped Schiff base complexes. The uniqueness of III lies in the incorporation of a metal atom in the fly-over chain.

Compound III is unique in other ways. Unlike most known bi- and polymetallic complexes which contain metal–metal bonds[15] or show strong metal–metal interactions through bridging ligands,[16–18] the metal atoms in III are remote, exist in strongly

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(4) **trans-[[[*cis*-Tetracarbonylbis(*N*-((2-diphenylphosphinamido)ethyl)-salicylaldimino-*P*)]molybdenum(0)]-*N*,*N*′,*O*,*O*′]nickel(II)** (II). A mixture of complex I (0.90 g) and 0.25 g of nickel acetate tetrahydrate (0.25 g) in dry tetrahydrofuran (25 mL) was stirred at room temperature for 1 day. Evaporation of the solvent and addition of an equal amount of cold methanol gave a crude product which was recrystallized from methanol to yield 0.83 g (84%) of the pure bimetal product as the 0.5-methanol solvate. The presence of methanol was detected by $^1H$ NMR. Anal. Calcd for $C_{46}H_{40}N_4NiO_6P_2 \cdot 0.5CH_3OH$: C, 57.14; H, 4.33; N, 5.73. Found: C 57.09; H, 4.50; N, 5.56.

(5) Crystals of III suitable for the structural determination were grown at 40 °C by slow evaporation of a 1:1 THF/$CH_3OH$ solution. The crystal structure was determined by the heavy atom method, as previously described.[6] Space group $P2_1/c$, $Z = 4$, $a = 21.350$ (9), $b = 10.574$ (3), $c = 22.705$ (9) Å; $\beta = 106.99$ (2)°; $\rho_{obsd} = 1.28$, $\rho_{calcd} = 1.30$ g cm$^{-3}$; $R = 5.6$, $R_w = 6.4\%$ (refinement continuing) for 3431 reflections ($\geq 3\sigma(I)$; Mo K$\alpha$ radiation: data/parameter ratio = 6.04). Absorption corrections were carried out; H atoms were included. Tables of atomic parameters and structure factors are available as supplementary material. Full details will be published elsewhere.

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dissimilar oxidation states, and reside in distinctly different ligand environments. The molybdenum atom is in a low valent state and is surrounded by a soft ligand field. The divalent nickel ion is surrounded by a hard ligand field. To our knowledge, there is no comparable analogous bimetal complex known. Metalla-β-diketonato complexes contain two transition metals in different ligand fields but can interact through the π system.[19] The recently reported zirconocene phosphines[20] are able to bind two different metals remotely, but both ligand sites are soft. A major impetus for the synthesis and characterization of bimetal complexes containing greatly dissimilar metal sites is the search for simple systems which might permit the controlled reduction of CO and $N_2$.[21,22]

**Supplementary Material Available:** A listing of positional and thermal parameters and structure factors (19 pages). Ordering information is given on any current masthead page.

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# Formation of Chromium Carbene Ions by Reaction of Electronically Excited Chromium Ions with Methane in the Gas Phase

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*Contribution No. 6307 from the*
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*Received October 6, 1980*

The gas-phase reactions of singly charged chromium ions have been studied by using an ion beam tandem mass spectrometer[1] equipped with two different ion sources. One source produces singly charged chromium ions by thermal decomposition of $CrCl_3$ and surface ionization of the resulting Cr on a hot rhenium surface.[1] It is estimated that at the filament temperature used, ~2350 K, more than 99% of the chromium ions are in the $^6S$ ground state. The other source forms $Cr^+$ from $Cr(CO)_6$ by electron impact.[2] The metal ions are collimated, mass and energy selected, and allowed to interact with the target gas in a collision chamber. Product ions scattered in the forward direction are detected by using a quadrupole mass spectrometer.

Using the suface ionization source, chromium carbene ions are formed in the *endothermic* reactions of $Cr^+$ with ethylene and cyclopropane, processes 1 and 2. Analysis of the thresholds[3] yields

$$Cr^+ + C_2H_4 \rightarrow CrCH_2^+ + CH_2 \qquad (1)$$

$$Cr^+ + \text{cyclo-}C_3H_6 \rightarrow CrCH_2^+ + C_2H_4 \qquad (2)$$

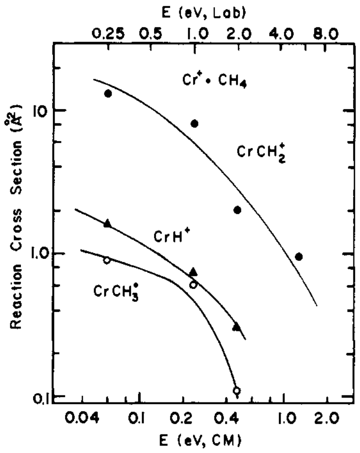


**Figure 1.** Variation in experimental cross section for the reactions of $Cr^+$ with methane as a function of kinetic energy in the center-of-mass frame (lower scale) and laboratory frame (upper scale). For the results illustrated, $Cr^+$ was produced by 30-eV electron impact from $Cr(CO)_6$.

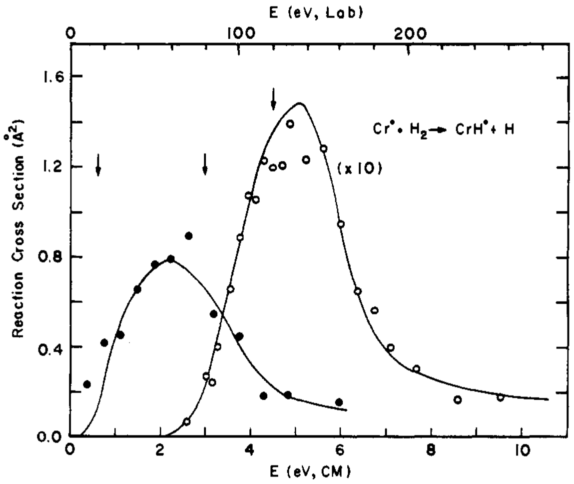
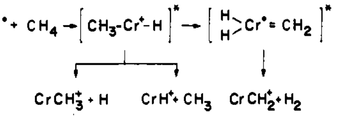


**Figure 2.** Variation in experimental cross section for reaction 3 as a function of kinetic energy in the center-of-mass frame (lower scale) and the laboratory frame (upper scale). Open circles depict data for beam of surface-ionized $Cr^+$, while closed circles depict data for $Cr^+$ produced by 30-eV electron impact from $Cr(CO)_6$. Curves drawn are theoretical fits to the data as described in ref 9. Arrows depict derived thresholds of 3.0 and 0.6 eV, and the bond energy of $H_2$, $D$ = 4.5 eV.

Scheme I



a chromium carbene bond strength, $D°(Cr^+-CH_2) = 65 \pm 7$ kcal/mol.[4] Reaction of $Cr^+$ with methane yields $CrH^+$ as the only detectable product at high energies.

Surprisingly, $Cr^+$ formed by electron impact from $Cr(CO)_6$ reacts with methane to produce $CrCH_2^+$ in abundance, and the behavior of the cross section as a function of energy (Figure 1) is characteristic of an *exothermic* reaction. Also observed are lesser amounts of $CrCH_3^+$ and $CrH^+$.[5] A mechanism for the formation of these products is suggested in Scheme I. On the basis of the measured bond energy, formation of $CrCH_2^+$ from reaction with $CH_4$ is endothermic by 45 kcal/mol.[6] Since the

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(1) For a more detailed description of the instrument, see: Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *50*, 21.

(2) This new source is of standard design in which an ion beam is extracted at right angle from a collimated electron beam.

(3) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.*, in press.

(4) This value can be compared to other metal ion–carbene bond energies. (a) $D°(Mn^+-CH_2)$ is between 92 and 100 kcal/mol: Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449. (b) $D°(Co^+-CH_2) = 85 \pm 7$ kcal/mol.[3] (c) $D°(Ni^+-CH_2) = 86 \pm 6$ kcal/mol: Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L., unpublished results. In general, threshold experiments yield only a lower limit for the bond strength. However, studies with $Co^+$ (ref 3), which include results for $CoCH_2^+$ formed in *both* endothermic and exothermic processes, suggest that the threshold data yield the true bond energies rather than a lower limit.

(5) Analysis of the thresholds of the reactions of $Cr^+$ formed by surface ionization with $H_2$ and ethane yield, respectively, $D°(Cr^+-H) = 35 \pm 5$ kcal/mol and $D°(Cr^+-CH_3) = 37 \pm 7$ kcal/mol. Reactions forming these species from methane are thus endothermic by 69 and 67 kcal/mol, respectively.

(6) $\Delta H_f°(CH_4) = -17.9$ kcal/mol from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1975. $\Delta H_f°(CH_2) = 92.4$ kcal/mol from: Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data Suppl.* **1975**, *4*, No. 1.

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