Tamborski[5] as synthesized by reaction $C_6F_5MgBr + CoBr_2 \rightarrow (C_6F_5)_2Co$ in THF, was isolated by them as a blue powder (ether solvated). In our reaction sequence, the Co vapor-C_6F_5Br codeposition is carried out at −196 °C followed by warmup, pumpoff of excess C_6F_5Br, and washing the residue with pure deoxygenated toluene yielding a dark red-orange product that then contained bonded toluene (**2**).

Hydrolysis of this product yielded Co salts and C_6F_5H in a 1:2 ratio, whereas addition of triethylphosphine yielded bis(*F*-phenyl)bis(triethylphosphine)cobalt(II) (**3**) with release of toluene.

$$\begin{tikzcd}
1 + C_6H_5CH_3 \arrow[r, "\text{in}", "\text{reactor}"'] & (\eta^6\text{-}C_6H_5CH_3)Co(C_6F_5)_2 \\
 & \mathbf{2} \arrow[dl, "PEt_3"'] \arrow[ddl, "H_2O"] \\
(C_6F_5)_2Co(PEt_3)_2 + C_6H_5CH_3 & \\
\text{Co salts} + C_6F_5H + C_6H_5CH_3 &
\end{tikzcd}$$

An x-ray structure determination of the crystals grown in toluene (**2**) was undertaken. This compound crystallizes with four molecules of $[\eta^6\text{-}C_6H_5CH_3(C_6F_5)_2Co]$ in an orthorhombic unit cell belonging to space group *Pnma*. The lattice constants are $a = 11.465$ (9), $b = 16.025$ (12), and $c = 9.503$ (8) Å. The structure was solved using Patterson and Fourier techniques and refined by full-matrix least squares using 1335 diffractometer data (λ 0.7107 Å) observed in the range $\sin\theta/\lambda \leq 0.626$. Refinement of the asymmetric unit of structure, including coordinates for the hydrogen atoms obtained from a difference synthesis and anisotropic parameters for all other atoms, produced an *R* value of 6.1% and a weighted *R* of 5.8%.

The molecular structure, depicted in Figure 1, consists of a cobalt atom σ bonded to two *F*-phenyl ligands and π-bonded to one toluene ligand. The $Co\text{-}C_1$ σ bond distance is 1.931 (5) Å and the C_1CoC_1' bond angle is 88.3 (3)°. The Co atom is 1.627 (2) Å from the plane of the toluene ligand and the average Co-C π-bond distance of 2.141 (7) Å is similar to the results found in $(C_6H_5)CCo_3(CO)_6\cdot\pi\text{-}C_6H_3(CH_3)_3$ of 2.15 (3) Å.[7] The toluene ligand makes an angle of 86.3° with the plane defined by cobalt and the two σ-bonded carbons.

The molecule has *m* (*Cs*) symmetry which is fully utilized crystallographically. The carbon framework of both *F*-phenyl ligands remains planar and the normal trend in bond angles for electron releasing and withdrawing substituents is observed.[8] Carbon-carbon bond lengths in the *F*-phenyl ligand average 1.373 (8) Å and the observed C-F distance is 1.349 (7) Å. The average C-C length in the toluene ligand is 1.391 (8) Å.

Formally this compound is a 17-electron five-coordinate system. It is paramagnetic. As far as we are aware, this is the first example of a η^6-arene complex of an R_2M compound. It does open up many possibilities involving π-complexation to simple R_2M compounds, particularly of the metals Co, Ni, and Pd. Indeed, we have produced another similar "coordinatively unsaturated species" CF_3PdI that also tends to coordinate toluene, although more weakly.

In a typical experiment about 50 ml of *F*-bromobenzene (C_6F_5Br, 40 mmol) is placed in a sample inlet tube and freeze-thaw degassed. An aluminum oxide coated tungsten wire wound crucible (Sylvania Emissive Products, CS-1002A) is charged with about 1 g of Co metal pieces, weighed, and placed in position. The crucible in the metal atom reactor system[6] is warmed to dull red heat for 10-15 min. The reactor is then cooled to −196 °C and a coat of about 3 g of substrate is inletted. The crucible is slowly warmed until the metal melts at which time it may be necessary to decrease heat to avoid splattering. After a good vaporization rate is attained (35-45 A, 6-6.5 V) substrate is continually inletted resulting in a deep red matrix. After about 1 h the reaction is stopped and the reactor warmed to room temperature (about 0.5 g of Co or 8 g-atoms evaporated with all substrate inletted). The excess substrate is transferred under vacuum with stirring to a −196 °C on a vacuum line. The reactor is pressured to atmospheric with nitrogen, and with nitrogen flushing the contents are washed with five 25-ml portions of dry deoxygenated toluene by means of a syringe and long Teflon needle with magnetic stirring. The combined washings are filtered in inert atmosphere Schlenk ware employing filter paper or a D-porosity (10-25 μ) fritted filter. The solution is concentrated by solvent evaporation, and then with cooling in a −78 °C bath crystals are formed. However, it is imperative that throughout these manipulations stopcock grease entering the solution be avoided, or a dark oil results. The crystals are filtered and collected under nitrogen (yield about 10% based on cobalt evaporated).

Bis(pentafluorophenyl)-η^6-(toluene)cobalt(II) forms dark orange red colored crystals that are air sensitive. The crystals darken at 92° and melt at 133-138°. Ir (Nujol/Fluorolube mulls, cm^{-1}) 3100 (w), 2930 (w), 2860 (w), 1635 (m), 1610 (w, sh), 1542 (m, sh), 1438 (m, sh), 1508 (vs), 1463 (vs), 1455 (vs, sh), 1440 (vs, sh), 1386 (s), 1360 (s), 1355 (s, sh), 1320 (w, sh), 1278 (m), 1258 (w, sh), 1040 (s, sh), 998 (s), 995 (vs), 915 (s), 868 (w), 811 (s), 780 (s). The crystals, dissolved in toluene, react with triethylphosphine to yield light yellow-green crystals of bis(*F*-phenyl)bis(triethylphosphine)cobalt(II) which discolors at 100°, dec 135°.

Acknowledgment. Generous financial support of the National Science Foundation (GP-42376) is greatly appreciated. L.J.R. also is grateful for a University of North Dakota Faculty Research Grant.

Supplementary Material Available: Tables of observed and calculated structural factors are available (7 pages). Ordering information is given on any current masthead page.

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Received May 10, 1976

Isocyanide Insertion Rearrangements and Their Bonding to Transition Metal Atoms

Sir:

Considerable effort has now been expended in the study of carbonyl insertion rearrangements in organometallic compounds.[1] While similar rearrangements have been observed for a variety of other small molecules, in many cases, the scope, mechanisms, and bonding details have not been fully established.[2] We report, here, results of our investigations of the reactions of cyclopentadienyl group 6 organometallic anions containing isocyanide ligands[3] with methyl iodide. They reveal a characteristic pattern of facile isocyanide insertions and demonstrate novel modes of attachment of the inserted fragments to the metal atoms.

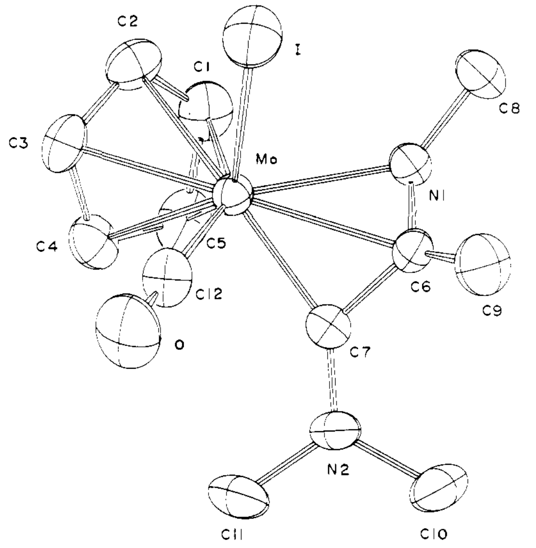


Figure 1.

Table I. Pertinent Bond Distances and Angles of the Imino-Dimethylamino Carbene Ligand

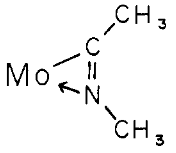
Atoms	Distance, Å	Atoms	Angle, deg
Mo-C6	2.354 (5)	C7-C6-N1	109.7 (4)
Mo-N1	2.257 (4)	C6-C7-N2	127.8 (5)
Mo-C7	2.027 (5)	C6-N1-C8	118.4 (5)
C6-C7	1.455 (7)	C9-C6-N1	126.3 (5)
C6-N1	1.332 (6)	C7-C6-C9	123.6 (5)
C7-N2	1.305 (6)	C7-N2-C10	123.3 (5)
C6-C9	1.504 (8)	C7-N2-C11	120.7 (5)
N1-C8	1.457 (7)	C10-N2-C11	115.8 (5)
N2-C10	1.464 (7)		
N2-C11	1.453 (7)		

The reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$ with methyl iodide in THF at room temperature produces a dark red compound that can be chromatographically purified. Its formula, $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2(CH_3)_2I$, was established by a combination of mass spectrum (parent ion, *m/e* 428) ^{1}H NMR, ir, and elemental analyses. The molecular structure was provided by a x-ray crystal structure analysis.[4,5] The structure was solved by conventional Patterson and Fourier techniques. Refinement converged after three cycles of anisotropic least-squares refinement on all nonhydrogen atoms and coordinate refinement on all 17 located hydrogen atoms. Reflections (1803) with $F_o^2 > 3\sigma(F_o^2)$ yielded the conventional reliability factors $R = 0.025$ and $R_w = 0.027$. The structure is shown in Figure 1. A normal $\eta^5\text{-}C_5H_5$ ring, CO group, and iodide atom are accompanied by an imino-dimethylamino carbene unit in bonding to the metal atom. To achieve an 18-electron configuration around the metal atom, the imino-amino carbene acts as a four electron donor. Two of these electrons are provided by the carbenoid carbon, C7, and two by the imino function, C6-N1.

The bonding within this imino-dimethylamino carbene grouping shows no unusual distortions. Pertinent bond distances and angles are listed in Table I. Of primary interest is the mode of bonding of the imine group C6-N1 to the metal atom. In similar systems it has previously been assumed that the attachment of such imine groups occurs via coordination of the lone pair of electrons on the nitrogen atom.[6] In this case, the short Mo to C6 and N1 distances together with the skewed attachment to the metal atom indicate a major if not predominant interaction of the metal atom with the imine π bond.[7]

The most plausible mechanism of formation involves: (1) an initial methylation of the anion at the molybdenum atom, (2) two sequential isocyanide insertions, which are most likely promoted by the solvent and one iodide ion,[8] (3) rearrangement and incorporation of the more remotely positioned imine function into the bonding sphere of the metal atom, and (4) methylation of the other imine group at the nitrogen atom. This last step produces the dimethyl amino unit.

Evidence supporting this mechanism is provided by several related reactions. Reactions of the molybdenum-isocyanide anions with chloroacetonitrile give complexes in which the insertion resistant CH_2CN unit is bonded to the molydenum atoms.[3] Reaction of $(\eta^5\text{-}C_5H_5)W(CO)_2CNCH_3^-$ with methyl iodide yields $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)CH_3$, ν(CO) 1915, 1810 cm^{-1}; ν(CN) 2120 cm^{-1}, in which the methyl group is attached to the insertion resistant tungsten atom.[1a,10] Finally, treatment of $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3^-$ with methyl iodide produces the compound $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3CH_3)$.[10] Its infrared spectrum shows two carbonyl absorptions at 1930 and 1825 cm^{-1} and a weaker absorption at 1720 cm^{-1}. The latter absorption cannot be attributed to a terminal isocyanide ligand and is at a significantly higher energy position than normal iminoacyl absorptions.[11] We propose that, in this case, an isocyanide insertion has occurred, but in order to satisfy the electron requirements of the metal atom, it π-bonds as a three-electron donor, structure I. In this sense, then, it should resemble a π-coordinated acetylene, and this could explain the higher CN vibration. A structure analysis is planned and should provide the final details of this bonding arrangement.



I

In addition, this compound reacts with tetracyanoethylene, TCNE, to form the adduct $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3CH_3)\cdot TCNE$.[10] This causes displacement of two electrons of the imino donor from the metal atom. It, then, bonds as a normal iminoacyl unit, and even in the presence of this additional and strongly electron withdrawing TCNE ligand,[12] the imine vibrational frequency lowers to 1630 cm^{-1}.

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

Supplementary Material Available: Structure factors, atomic coordinates, and thermal parameters (13 pages). Ordering information is given on any current masterhead page.

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(4) Space group = $P\bar{1}$; $a = 8.296$ (4), $b = 7.492$ (4), $c = 13.945$ (8) Å; $\alpha = 85.95$ (4), $\beta = 72.01$ (3), $\gamma = 63.46$ (3)°; $Z = 2$; Radiation = Mo $K\alpha_1 = 0.7093$

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be approximately 0° if the Mo atom were bonded solely to the nitrogen lone pair or 90° if it were bonded to the imine π bond.

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Received February 26, 1976

Novel Chiral Triorganotin Halides. Stabilization of Optically Active Tin Centers by Intramolecular Coordination

Sir:

Contrary to the high optical stability of tetraorganotin compounds[1] triorganotin halides are configurationally unstable.[2,3] In the presence of nucleophiles the RR′R″SnX enantiomers isomerize either via formation of penta- or hexacoordinate tin intermediates which are stereochemically nonrigid or via an SN2 type mechanism which leads to direct inversion of configuration.[4]

We report here that chiral triorganotin halides with high optical stability may be obtained by rendering the tin atom pentacoordinate by intramolecular coordination so that stereoisomerization pathways are blocked.

Recently, we have reported[5] a facile one-step synthesis for $(2\text{-}Me_2NCH_2C_6H_4)R_2SnBr$ compounds (**1**, R = Me; **2**, R = Ph). An x-ray investigation has shown that the tin atom in **2** is pentacoordinate as a result of intramolecular Sn-N coordination.[6]

We have now synthesized[7] $(2\text{-}Me_2NCH_2C_6H_4)MePhSnBr$, **3**, in which the tin atom is a chiral center. The Me_2NCH_2 ligand, present in this structure, allows the study by NMR spectroscopy of the configurational stability of the chiral tin center as well as of the occurrence of intramolecular Sn-N coordination.[8]

Figure 1 shows the NMR spectrum of **3** in toluene-d_8 at 10, 30, and 123 °C. The benzylic protons (25 °C;[9] AB, δ 3.02 and 2.81 ppm) are anisochronous up to 123 °C[10] ($\Delta\delta$ decreases from 21 Hz (0 °C) to 15.5 Hz (123 °C)) and thus diastereotopic. Consequently, up to 123 °C the rate at which the absolute configuration of the chiral tin atom inverts (Sn ⇄ nƧ) is slow on the NMR timescale, because it is only by this inversion process that the benzylic protons become enantiotopic and isochronous.

The observation below 30 °C of two singlets for the NMe protons at δ 1.50 and 1.28 ppm which coalesce above 30 ° to one singlet at 1.39 ppm is interpreted in terms of rate determining intramolecular Sn-N coordination. Pyramidal inversion at nitrogen in *N,N*-dialkylbenzylamines is a low energy process which has an estimated barrier lower than 6 kcal/mol.[11] Consequently, inversion at nitrogen (rate constant k_i) takes place in the tetracoordinate tin conformer. In the pentacoordinate tin conformer Sn-N coordination (rate constant k_c) makes a stable prochiral assembly of the NMe_2 group and renders the NMe groups diastereotopic and thus anisochronous because of the dissymmetry at tin. Two processes can be envisaged by which the NMe groups can become homotopic (enantiotopic): (i) by inversion of configuration at tin in the pentacoordinate conformer (rate constant k_r'), i.e., without prior Sn-N bond dissociation (vide infra), and (ii) by Sn-N bond dissociation (rate constant k_d) followed by inversion at N with concomitant 180 ° rotation about the CH_2-N bond and re-formation of the Sn-N bond. The latter mechanism accounts for the observed dynamic NMR pattern whereas the observation that the NCH_2 and NMe proton resonance patterns coalesce at different rates excludes the former mechanism.

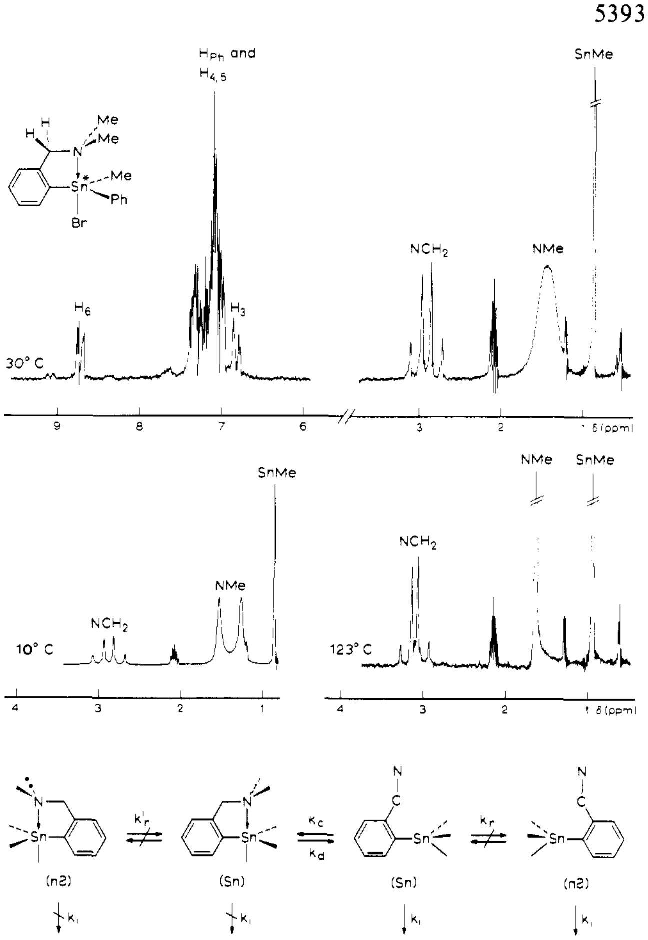

Figure 1. ^1H NMR spectrum (100 MHz) of $(2\text{-}Me_2NCH_2C_6H_4)(C_6H_5)MeSnBr$ in toluene-d_8 (resonances at δ 2.1 and 7.1 ppm are due to hydrogen containing sites of the solvent). Only the high field part of the spectra recorded at 10° and 123 °C is shown.

External ligands such as PPh_3, NPh_3, DABCO, and pyridine, which readily cause inversion of configuration in other chiral triorganotin halides,[1,2] do not interact with the tin atom in **3**[12] as can be concluded from the absence of any effect on the resonance patterns or on the T_c value of the NMe resonances. However, it has been shown that in $(2\text{-}Me_2NCH_2C_6H_4)_2MeSnBr$, **4**,[13] which contains two internal ligands, intramolecular exchange does take place. The NMR of **4** at −50 °C shows two sets of diastereotopic NCH_2 protons (two AB patterns: $\Delta\delta$, 1.48 ppm, irradiation at 2.7 ppm resulted in a singlet at 4.27 ppm; $\Delta\delta_2$ 0.58 ppm), two multiplets for H_6 at δ 8.85 and 7.20 ppm, and two sets of NMe protons (two singlets at δ 1.34 and 1.52 ppm for diastereotopic NMe groups and one singlet at 1.62 ppm for homotopic NMe groups) (Figure 2). This pattern is compatible with a pentacoordinate structure at low temperature containing one C,N- and one C-bonded $2\text{-}Me_2NCH_2C_6H_4$ group. In the temperature range −50° to 20 °C the two sets of resonance patterns for the $2\text{-}Me_2NCH_2C_6H_4$ groups coalesce to give an averaged multiplet for H_6 at δ 8.12 ppm, one broadened singlet for the NMe protons at the position of homotopic NMe groups while the two sets of diastereotopic NCH_2 protons coalesce to an averaged AB pattern with $\Delta\delta$ 0.58 ppm. The two types of $Me_2NCH_2C_6H_4$ groups observable below −50 °C have now become equivalent on the NMR timescale by an intramolecular exchange process (pentacoordinate Sn ⇄ pentacoordinate