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 (12) The spectra obtained by Gainulin et al.⁹ for species in solution are very similar to those reported in the present study but the assigned coupling constants differ vastly. For compound 1, the assignment of Gainulin et al. is $a_N = 5.0 \pm 0.2$ and $a_H = 2.5 \pm 0.2$. Placing these values in our simulation program leads to a spectral pattern similar to that found experimentally. Mathematically either assignment fits the observed spectrum. Upon *N*-methyl substitution, Gainulin et al. note that a_N decreases to 2.8 G. We confirm this experimental result with isolated complexes but, in view of our assignment of a_N , we note that *N*-CH₃ substitution increases a_N by a small amount. This is certainly a more reasonable result than nearly doubling the constant when H is substituted by CH₃. Proof for our assignment comes from studies on the N-D system discussed in the text.
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 (15) Frozen glass spectra reveal the complexes to have rhombic or axial *g* tensors with overall *g* spread of less than 0.03. Unfortunately, neither ¹H nor ¹⁴N superhyperfine splittings have been clearly resolved in the frozen glass spectra, the analysis of which will be reported in detail in the full paper.
 (16) Russian workers^{8,9,17} seem to be acutely aware of these temperature effects and often report highly resolved EPR spectra at odd and seemingly arbitrary temperatures. It was from scrutiny of their experimental results that it first occurred to us to vary the temperature of samples.
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 (18) In support of this argument, we note that ²H splitting is not resolved in Mo enzymes when ²H is substituted for ¹H. The estimated ²H splitting is of the same magnitude as ¹⁴N splittings found in Mo(V) complexes² and therefore the lack of resolution of ¹⁴N splitting in Mo enzymes is not at all unexpected.

Narayanankutty Pariyadath, W. E. Newton, Edward I. Stiefel*

Contribution No. 571
 Charles F. Kettering Research Laboratory
 Yellow Springs, Ohio 45387
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Metal Atom Synthesis of

η^6 -Toluenebis(*F*-phenyl)cobalt(II)

$[\eta^6\text{-C}_6\text{H}_5\text{CH}_3(\text{C}_6\text{F}_5)_2\text{Co}]$, a New Type of

π -Arene Complex. X-Ray Structure Determination

Sir:

Simple RMX and R₂M compounds of transition metals such as Fe, Co, Ni, Pd, or Pt have been of interest to quite a number of workers.¹ We have found that the "metal atom technique"² (metal vapors condensed with organic compounds) has been

Table I. Atomic Coordinates^a

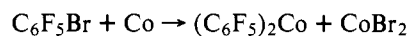
Atom	Coordinates		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
Co	1949 (1)	2500	-74 (1)
C ₁	969 (4)	1660 (3)	778 (5)
C ₂	1183 (5)	1340 (3)	2090 (6)
C ₃	493 (6)	745 (4)	2732 (6)
C ₄	-475 (6)	460 (4)	2051 (7)
C ₅	-729 (5)	750 (4)	729 (7)
C ₆	-5 (4)	1343 (3)	138 (6)
F ₂	2133 (3)	1598 (2)	2824 (3)
F ₃	752 (4)	450 (3)	4022 (4)
F ₄	-1174 (4)	-106 (2)	2668 (5)
F ₅	-1663 (3)	462 (2)	39 (5)
F ₆	-2829 (3)	1601 (2)	-1181 (4)
C ₇	2498 (7)	2500	-2271 (8)
C ₈	2821 (5)	1760 (4)	-1605 (7)
C ₉	3472 (5)	1764 (5)	-354 (7)
C ₁₀	3815 (7)	2500	260 (11)
C ₁₁	1784 (10)	2500	-3611 (9)
H ₈	2584 (63)	1323 (40)	-1919 (74)
H ₉	3641 (59)	1208 (38)	99 (66)
H ₁₀	4149 (86)	2500	1093 (100)

^a Estimated standard deviations are given in parentheses for least significant digit.

quite useful for preparation of some of the simple nonligand stabilized RMX compounds in the absence of complicating donor solvents.³ Due to the extraordinary robustness of the R_f-M bond,⁴ the CF₃I and C₆F₅Br reactants have been quite useful to us in terms of production of stable, characterizable RMX compounds.



We report here the production of a stable R₂Co compound utilizing the metal atom technique. This compound is formed in the reaction of *F*-bromobenzene with cobalt atoms, and is the first example of an R₂M compound produced by the method.



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Bis(*F*-phenyl)cobalt(II) (1), previously reported by Smith and

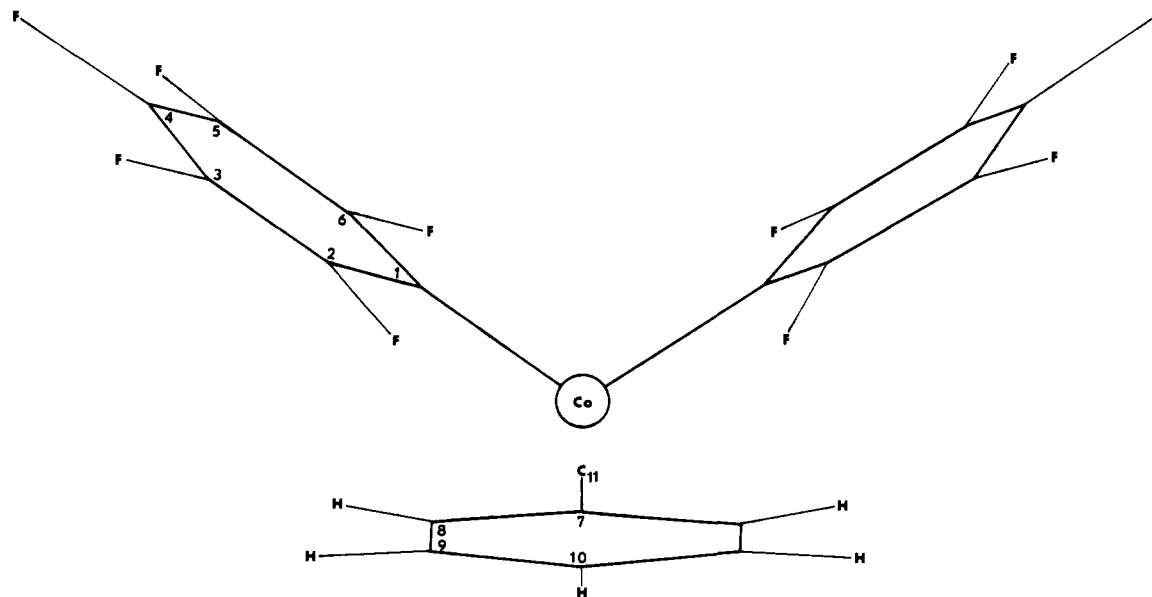
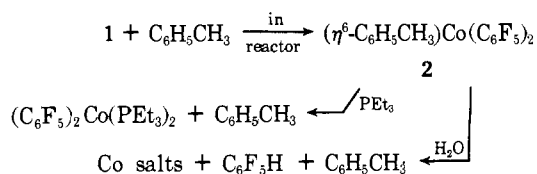


Figure 1. The structure of $[\eta^6\text{-C}_6\text{H}_5\text{CH}_3(\text{C}_6\text{F}_5)_2\text{Co}]$. The crystallographic mirror plane contains Co, C₇, C₁₀, C₁₁, and H₁₀.

Tamborski⁵ 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 $-196^\circ C$ 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.



An x-ray structure determination of the crystals grown in toluene (**2**) was undertaken. This compound crystallizes with four molecules of $[\eta^6-C_6H_5CH_3(C_6F_5)_2Co]$ 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 ($\lambda 0.7107$ 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- 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 $(C_6H_5)CCO_3(CO)_6\pi-C_6H_3(CH_3)_3$ 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* (C_s) 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 system⁶ is warmed to dull red heat for 10-15 min. The reactor is then cooled to $-196^\circ C$ 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 $-196^\circ C$ 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 $-78^\circ C$ 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 $133-138^\circ$. 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° .

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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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**B. B. Anderson, C. L. Behrens
L. J. Radonovich,* K. J. Klabunde***

*Department of Chemistry, University of North Dakota
Grand Forks, North Dakota 58202*

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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 ligands³ 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.