Figure 1. Stereochemistry of the 2-[IrBr₂(CO)(PMe₃)₂]B₅H₈ molecule. [ORTEP diagram, 50% ellipsoids for non-hydrogen atoms and artificial 0.1 Å radius spheres for pentaboranyl hydrogen atoms.]

hydride (ν_{CO} = 2085, ν_{IrH} = 1985 cm⁻¹) was observed,[4] which slowly decayed to **2**. The observation of the intermediate IrClH(CO)(PMe₃)₂(BrB₅H₇) (*vide infra*) of undetermined stereochemistry shed no light on the formation of only the 2-metalated isomer of **2**. It did, however, suggest that oxidative addition of BH may be a facile, reversible process.

Subsequently, we found that excess B₅H₉ reacted with **1** (but not with *trans*-IrCl(CO)(PPh₃)₂) in hexane at −45°, yielding colorless 2-[IrClH(CO)(PMe₃)₂]B₅H₈ (**3**) in 80% yield: ir (Kel-F and Nujol mulls) 2573 (m, ν_{BH}), 2555 (m, ν_{BH}), 2082 (s, ν_{CO}), 1978 (s, ν_{IrH}), and 945 cm⁻¹ (s, δ apical BH); mp 64° dec (rapid heat); ¹H {¹¹B} nmr³ (−30°, CD₂Cl₂) 6.9 (t, 1, IrH, J_{PIrH} = 20 Hz), 1.4 (s, 2, μ$_{BH}$), −0.1 (s, 2, μ$_{BH}$), −1.4 (s, 1, B(1)H), −2.8 (t, 18, PCH₃, J_{PCH} = 4.2 Hz); ³¹P {¹H} nmr (−70°, CH₂Cl₂) 4.0 (s). **3** slowly decomposes at 25°, but may be kept indefinitely at −20°. The reaction is at least partially reversible, since pyrolysis of **3** at 150° gave a 38% yield of B₅H₉.

The molecular stereochemistry of **2** has been determined unambiguously *via* a three-dimensional X-ray structural analysis.

The species crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (no. 14; C_{2h}^5) with a = 13.824 (4) Å, b = 10.661 (3) Å, c = 13.611 (3) Å, β = 104.90 (2) Å, ρ_{obsd} = 2.01 (1) g cm⁻³, ρ_{calcd} = 2.036 g cm⁻³ for Z = 4, and molecular weight = 594.305. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer, using Mo Kα radiation and a θ–2θ scan technique. All data were corrected for absorption (μ = 118.16 cm⁻¹). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the final discrepancy indices being R_F = 4.64% and R_{wF} = 4.25% for the 2546 independent reflections representing data complete to 2θ = 45°. All atoms other than the methyl hydrogens have been located, the determined molecular stereochemistry being shown in Figure 1.

The crystal consists of an ordered racemic array of 2-[IrBr₂(CO)(PMe₃)₂]B₅H₈ molecules in which the iridium atom is *in* a fairly regular octahedral coordination environment. (Angles between mutually cis ligands

(4) This hydride could also be detected *via* ¹H nmr (*cf.* ref 3b).

range from 86.1 (1) to 93.5 (4)°, while angles between trans ligands vary from 172.2 (1) to 177.8 (4)°.)

The iridium–phosphorus distances are equivalent, with Ir–P(1) = 2.362 (3) and Ir–P(2) = 2.361 (3) Å. Iridium–bromine distances are, however, decidedly nonequivalent, with Ir–Br(1) = 2.638 (1) and Ir–Br(2) = 2.516 (1) Å. (Note that the pentaboranyl ligand exerts a stronger trans-lengthening influence than does the carbonyl ligand!) Other distances within the iridium(III) coordination sphere are Ir–CO = 1.95 (2) and Ir–B (2) = 2.07 (1) Å.

The pentaboranyl ligand is bonded to iridium *via* its basal (2−) position. B(1)–B(basal) distances range from 1.64 (2) to 1.69 (2) Å, while B(basal)–B(basal) distances vary from 1.80 (2) to 1.91 (2) Å. The eight hydrogen atoms of the 2-pentaboranyl ligand have been located and refined, resulting distances being B(1)–H(1) = 1.08 (8), B(basal)–H(terminal) = 1.08 (11)–1.55 and B(basal)–H(bridging) = 1.03 (10)–1.45 (10) Å.

It is of note that the strong trans influence[5] of the borane ligand, color[6] of the adducts, and carbonyl stretching frequencies[6] of the same indicate that a σ-bound pentaborane (9) unit is electronically similar to a σ-alkyl ligand.

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Organolanthanides and Organoactinides. X. Synthesis of a New Type of σ-Bonded Organolanthanide Complex: (η⁵-C₅H₅)₂LnC≡CPh

Sir:

In the past several years, there has been a revival of interest in the oganometallic chemistry of the actinides. One area which has received active interest has been the preparation of σ-bonded derivatives.[1−4] However, the lanthanides seem to have escaped investigation of this type. Their chemistry consists mainly of derivatives containing ionic π-bonded cyclopenta-

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(2) T. J. Marks, A. M. Seyam, and J. R. Kolb, *J. Amer. Chem. Soc.*, 95, 5529 (1973).
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Table I. Magnetic Susceptibilities[a,b]

Compound	Color	$10^6 \chi_m$, cgs	μ_{eff} (obsd)	Theor[13]
Yb	Orange	7,800	4.31	4.5
Er	Pink	39,000	9.64	9.6
Gd	Yellow	26,880	7.98	7.94

[a] Measured by the Faraday method at 300°K. [b] Estimated error is ±3%; values are corrected for diamagnetism.

dienyl[5] and cyclooctatetraenyl[6] ligands. The only well-characterized σ-bonded derivatives presently known are the Yb and Lu tetrakis(2,6-dimethylphenyl) derivatives, isolated as lithium salts.[7] We wish to report the preparation of a new class of organolanthanide compounds, $(\eta^5\text{-}C_5H_5)_2LnC{\equiv}CPh$ (Ph = phenyl; Ln = Gd, Er, and Yb). The Gd and Er derivatives represent the first examples of compounds containing a σ-bonded organic moiety bound to the respective metals.

These complexes are formed in good yields by the reaction of the particular $(\eta^5\text{-}C_5H_5)_2LnCl$[8] and lithium phenylacetylide[9] in THF at −20°. The compounds are purified by continuous extraction into benzene.[10] The compounds are destroyed by oxygen (though the Gd compound is stable in air for a few minutes) and both the phenylacetylide and cyclopentadienyl ligands are hydrolyzed by H_2O.

In the infrared spectra, all three compounds exhibit strong sharp C≡C stretches at ∼2050 cm⁻¹.[11] In addition, strong bands at 692 and 760 cm⁻¹ are characteristic of a monosubstituted phenyl group. The bands at 3100, 1450, 1010, and 775 cm⁻¹ are indicative of a η^5-bonded cyclopentadienyl moiety.[12]

The magnetic susceptibilities of the compounds are reported in Table I, and are indicative of the metal in the tripositive state.[13] One would not expect to see much deviation from these values as the 4f orbitals seem to be quite well shielded and should be perturbed only slightly by ligand fields.[14]

Visible spectra were taken for all of the complexes. The spectra of the erbium compound is interesting as it differs somewhat from the "free" Er^{3+} ion. The bands are broadened slightly and the values for ε are larger by over a factor of ten.[15,16] Bukietynska and Choppin[18]

suggested that changes of the intensity and shape of the hypersensitive[19] absorption band are due to the formation of inner-sphere complexes to a limited extent. High values can be related to the predominant existence of species in solution with low symmetries[20] and/or some degree of covalency. Since the symmetries in the starting material and products should be essentially identical, the observed enhancement lends support to these complexes being more covalent in nature. Also, a large charge transfer band is present which originates in the uv and extends into the visible region. This indicates that there is at least some interaction, other than strictly ionic, between the ligand and the metal. The origin of the charge transfer is probably ligand to metal.[6,21] However, this interaction need not be a large one to be observed. Also, it is not clear whether the electron is transferred into a 4f or 5d orbital.

The visible spectra of the Yb complex is uninformative as it is dominated by a large charge transfer band which is present in the $(\eta^5\text{-}C_5H_5)_2YbCl$ compound.[22] The Gd complex (an f^7 compound) is devoid of all transitions except for the charge transfer band as seen in the Er complex.

Though heretofore unknown for most lanthanides, the formation of metal–carbon σ bonds by our reaction scheme appears to be a general one and should work for other ligands and metals as well.[23,24] Further studies are in progress to elucidate the nature of the lanthanide–carbon σ bond.

(5) For a review, see (a) H. Gysling and M. Tsutsui, *Advan. Organometal. Chem.*, 9, 361 (1970); (b) R. G. Hayes and J. L. Thomas, *Organometal. Chem. Rev., Sect. A*, 7, 1 (1971).

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(8) R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Amer. Chem. Soc.*, 85, 672 (1963).

(9) Prepared from the reaction of *n*-butyllithium and ethynylbenzene in THF.

(10) All compounds gave satisfactory elemental analyses as performed by Schwarzkopf Microanalytical Laboratories. *Anal.* Calcd for $C_{18}H_{15}Yb$: C, 53.44; H, 3.73. Found: C, 53.10; H, 4.04. Calcd for $C_{18}H_{15}Er$: C, 54.24; H, 3.79; Er, 41.97. Found: C, 53.97; H, 3.82; Er, 41.60. Calcd for $C_{18}H_{15}Gd$: Gd, 40.47. Found: Gd, 40.56.

(11) In contrast, the C≡C stretch for ethynylbenzene comes at ∼2085 cm⁻¹.

(12) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91, 7281 (1969).

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(16) Values are also high compared with conventional coordination compounds; cf. ref 17.

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(18) K. Bukietynska and G. R. Choppin, *J. Chem. Phys.*, 52, 2875 (1970).

(19) Hypersensitive transitions are spectral bonds which exhibit substantial changes in intensity without a significant wavelength shift for very similar chemical environments.

(20) B. R. Judd, *J. Chem. Phys.*, 44, 839 (1966).

(21) J. C. Barnes, *J. Chem. Soc.*, 3880 (1964).

(22) This is the only lanthanide whose cyclopentadienide complexes do not correspond closely to the free ion.

(23) Preliminary results in our laboratories indicates this to be so.

(24) F. A. Hart, *et al.*, postulate[7] that lanthanide–carbon σ bonds are most favored for the heavier elements of this series. Maginn, *et al.*, also note[8] that they were only able to prepare $(\eta^5\text{-}C_5H_5)_2LnCl$ for the heavier lanthanides and that this was due to some subtle effect of the lanthanide contraction.

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Transverse Relaxation in Homonuclear Coupled Spin Systems

Sir:

It is often stated that for nonviscous liquids, nuclear spin–spin relaxation times (T_2) are equal to spin–lattice relaxation times (T_1) unless "slow" processes occur. This notion, which is based on an unwarranted extension of the Bloch equations, is incorrect for the general case of molecules with scalar coupling. Data presented here, together with a complete density matrix analysis,[1] show that the presence of homonuclear scalar coupling gives rise to T_2 values which are consid-

(1) R. L. Vold and R. R. Vold, to be submitted for publication.