from three iron atoms residing in the cluster which yields the observed EPR signal. Analyses of the 4.2 K spectra reveals two distinct sites with occupancy ratio of 2:1. We have described the data by the spin Hamiltonian ($S = \frac{1}{2}$)

$$\hat{H} = \beta\vec{S}\cdot\tilde{g}\cdot\vec{H} + \sum_{i=1}^{2}\{\vec{S}\cdot\tilde{A}(i)\cdot\vec{I}(i) - g_n\beta_n\vec{H}\cdot\vec{I}(i) + H_{quad}(i)\}$$

where i designates the two distinct sites. For details of such analyses see ref 8. The solid lines in Figure 2C,D are simulations using the parameters of Table I. The hyperfine tensors of the two types of Fe sites have different signs, an indication of a spin-coupled system.

Figure 2A shows a 4.2 K spectrum ($\Delta E_Q = 1.28$ mm/s and $\delta = 0.53$ mm/s) of a dithionite-reduced sample. In strong applied fields the spectra (not shown) exhibit magnetic hyperfine structure; i.e., the complex is paramagnetic with integer spin S.

The values for δ, which is a useful oxidation state marker, can be compared with those[4] of the Fe_4S_4 cluster produced by reconstitution of apo-Fd II. The average shift $\delta_{av} = 0.41$ mm/s of the oxidized Co–Fe cluster compares well with $\delta_{av} = 0.44$ mm/s of the $[Fe_4S_4]^{2+}$ cluster. Likewise, $\delta_{av} = 0.53$ mm/s of the reduced Co–Fe cluster is very similar to $\delta_{av} = 0.57$ mm/s observed[4] for $[Fe_4S_4]^+$. These observations, as well as the EPR results, suggest that a $[CoFe_3S_4]^{2+}$ cluster is isoelectronic with a $[Fe_4S_4]^+$ cluster.

In summary, the Mössbauer and EPR studies as well as chemical analysis suggest the presence of a novel cluster with a $CoFe_3S_4$ core. The formation of a $CoFe_3S_4$ cluster in Fd II shows that Fe_3S_4 clusters, incorporated into a protein matrix, can serve as promising precursors for the formation of novel clusters. We have preliminary evidence for the formation of a cluster containing copper.

(8) Christner, J. A.; Janick, P. A.; Siegel, L. M.; Münck, E. *J. Biol. Chem.* **1983**, *258*, 11157–11164.

Synthesis and X-ray Crystal Structure of the Stable Paramagnetic Dihydrido Complex Ir(H)$_2$(Cl)$_2$(P-*i*-Pr$_3$)$_2$[1]

Pasquale Mura

*Istituto di Strutturistica Chimica "G.Giacomello"
Area della Ricerca di Roma, CNR
C.P. N. 10 00016 Monterotondo Stazione (RM), Italy*
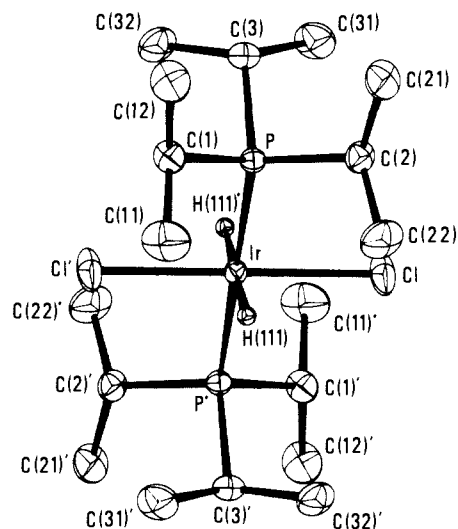
Received May 14, 1985

Paramagnetic transition-metal hydride complexes are very rare[2] and mainly characterized in solution.[3,4] To our knowledge only two complexes of tantalum[4] were stable enough in order to determine X-ray crystal structures.

Figure 1. Geometry of the Ir(H)$_2$(Cl)$_2$(P-*i*-Pr$_3$)$_2$ molecule with hydrogen atoms of the P-*i*-Pr$_3$ groups omitted for clarity. The Ir atom occupies the position of crystallographic symmetry $\bar{1}$. Relevant bond distances (Å) and angles (deg): Ir–H(111) = Ir–H(111)', 1.90 (7); Ir–Cl = Ir–Cl', 2.342 (1); Ir–P = Ir–P', 2.360 (2); Cl–Ir–H(111) = Cl'–Ir–H(111)', 93 (2); P–Ir–H(111) = P'–Ir–H(111)', 70 (2); Cl–Ir–P = Cl'–Ir–P', 90.27 (4); H(111)–Ir–H(111)', 180.0; Cl–Ir–Cl', 180.0; P–Ir–P', 180.0.

Paramagnetic iridium(IV) complexes are stable and have been extensively investigated.[5] Furthermore iridium easily forms hydrido compounds in the formal oxidation states I, III, and V.[6,7]

We now report the first example of a paramagnetic hydrido complex of Ir, i.e., the octahedral compound Ir^{IV}(H)$_2$(Cl)$_2$(P-*i*-Pr$_3$)$_2$ (1), Figure 1. To our knowledge, no other stable paramagnetic hydrido complexes of platinum group metals have been reported in the literature.

Ammonium hexachloroiridate [(NH$_4$)$_2$IrCl$_6$], when reacted with an excess of triisopropylphosphine in refluxing ethanol (containing concentrated HCl), gives 1 as deep-purple, air-stable microcrystals (yield 31% based on (NH$_4$)$_2$IrCl$_6$). Elemental analyses[8a] of monomeric[8b] 1 are consistent with the presence of two P-*i*-Pr$_3$ groups and two chlorine atoms. Its IR spectrum (KBr pellets) shows one band at 2003 cm^{-1} (m, w) attributed to ν(Ir–H).[9] In the far-IR spectrum 1 shows strong sharp band at 317 cm^{-1} indicating the presence of trans chlorine atoms.[10] The magnetic moment[11] of 1 at room temperature gives a value of 1.54 μ_B, in agreement with a spin-paired d^5 electron configuration (Ir(IV) low spin).[10,12] Thus 1 is a 17-electron hydride complex. For further experimental details see the supplementary material.

The geometry around the iridium atom is that of a slightly distorted octahedron, with three pairs of trans ligands P-*i*-Pr$_3$, Cl, and H.[13,14]

(1) Presented, in part, at the XIIth International Conference on Organometallic Chemistry, Vienna, Sept 8, 1985.

(2) (a) Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185–4192 and references cited therein. (b) Rhodes, L. F.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259–260 and references cited therein.

(3) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163–168 and references cited therein.

(4) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718–1726 and references cited therein.

(5) (a) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636–2641 and references cited therein. (b) Fergusson, J. E.; Rankin, D. A. *Aust. J. Chem.* **1983**, *36*, 863–869 and references cited therein. (c) Rankin, D. A.; Penfold, B. R., Fergusson, J. E. *Ibid.* **1983**, *36*, 871–883 and references cited therein. (d) Isobe, K.; Vazquez de Miguel, A.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 929–933 and references cited therein.

(6) For general reviews, see: (a) Muetterties, E. L., Ed. "Transition Metal Hydrides"; Marcel Dekker: New York, 1971. (b) Bau, R., Ed. *Adv. Chem. Ser.* **1978**, *No. 167*. (c) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1–82.

(7) Gomez, M.; Robinson, D. J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, 825–826 and references cited therein.

(8) (a) Satisfactory elemental analyses were obtained; see supplementary material. (b) Satisfactory molecular weight was obtained; see supplementary material.

(9) Attempts to obtain 1-d_2 led to extensive deuteration of the organic ligands, which overlapped with the Ir–D band.

(10) Bennet, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983–6994 and references cited therein.

(11) For magnetic measurements see supplementary material.

(12) Figgis, B. N. "Introduction to Ligand Fields"; Wiley: New York, 1966; pp 305–306.

Furthermore the ease of formation and high chemical stability of compound **1** indicates that more examples of such complexes may exist.

Acknowledgment. I am indebted to Prof. L. M. Venanzi for valuable suggestions and discussion and to Prof. B. Magyar for the molecular weight measurement.

Supplementary Material Available: (a) Experimental details including synthesis, elemental analyses, molecular weight measurement, and magnetic measurements, and (b) tables of final atomic coordinates and thermal parameters (4 pages). Ordering information is given on any current masthead page.

(13) $Ir(H)_2(Cl)_2(P-i-Pr_3)_2$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 8.191$ (3) Å, $b = 8.982$ (4) Å, $c = 16.447$ (4) Å, $\beta = 93.30$ (2)°, $V = 1208.0$ (7) Å³, ρ(calcd) = 1.61, ρ(meas) = 1.60 (1) g cm⁻³ (measured by flotation in $CdCl_2$ aqueous solution) for $Z = 2$ and $M = 585.66$. Iridium occupies a special position, that of crystallographic symmetry $\bar{1}$; the symmetric unit contains half of the molecule. Data collection was made by an automatic diffractometer Nicolet P3m (room temperature); the residuals for the 5237 data, corrected as described in ref 15 ($2\theta_{max} = 90°$; $I > 3\sigma I$; crystal size 0.13 × 0.23 × 0.68 mm) are $R = 3.12$ and $R_w = 3.60$. All the heavy atoms together with the 21 hydrogen atoms of the $P-i-Pr_3$ group were located and refined, hydrido hydrogen[16] contribution fixed.
(14) A full paper on this and related chemistry: Mura, P.; Segre, A. L., manuscript in preparation.
(15) Bachechi, F.; Zambonelli, L.; Marcotrigiano, G. *J. Cryst. Mol. Struct.* **1977**, *7*, 11–20.
(16) A difference-Fourier synthesis based on low-angle reflections[17] (with 458 reflections maximum sin $\theta/\lambda = 0.36$ Å⁻¹) clearly revealed the hydrido hydrogen position. Full-matrix refinement of all heavy atoms (anisotropic t.f.) and hydrido hydrogen (isotropic t.f.) with fixed contribution of 21 H atoms of the $P-i-Pr_3$ group gives $R = 1.58$ and $R_w = 1.80$ with Ir–H(111) 1.90 (7) Å and $B_{iso} = 1.7$ (2.1) Å².
(17) Bau, R.; Chiang, M. Y.; Ho, D. M.; Gibbons, S. G.; Emge, T. J.; Koetzle, T. F. *Inorg. Chem.* **1984**, *23*, 2823–2829 and references cited therein.

A New, Easily Accessible Reciprocal Chiral Stationary Phase for the Chromatographic Separation of Enantiomers

W. H. Pirkle* and Thomas C. Pochapsky

*School of Chemical Sciences
University of Illinois at Urbana-Champaign
Roger Adams Laboratory, Urbana, Illinois 61801*

N-Aryl-α-amino acids (and their ester and amide counterparts) contain a combination of π-donor, basic and acidic sites spatially arranged so as to afford unusually efficient chiral recognition upon interaction with the complementary π-acceptor, acidic and basic sites of *N*-(3,5-dinitrobenzoyl)-α-amino acids.[1,2] For example, the enantiomeric ω-undecenyl esters of *N*-(2-naphthyl)alanine are separable by HPLC on columns packed with a silica-bonded chiral stationary phase (CSP) derived from (*S*)-*N*-(3,5-dinitrobenzoyl)leucine, exhibiting an enantiomeric separability factor[4] of 10.4, an unusually large value. In view of the reciprocal aspect of chiral recognition, CSPs derived from *N*-(2-naphthyl)-α-amino acids were expected to afford facile separations of the enantiomers of *N*-(3,5-dinitrobenzoyl) derivatives of α-amino acids. Additionally, such CSPs were expected to separate the enantiomers of appropriately derivatized amines, amino alcohols, amino phosphonates, alcohols, and thiols. Appropriate derivatization consists of N, O, or S acylation with 3,5-dinitrobenzoyl chloride or 3,5-dinitrophenyl isocyanate.[6,7]

Scheme I[a]
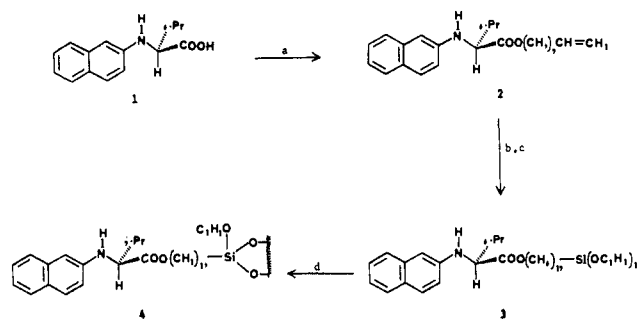
[a] (a) $CH_2=CH(CH_2)_9OH$ (1.1 equiv), CH_3SO_3H, toluene at reflux, azeotropic removal of water. (b) 1.5 g of **2**, 20 mL of $HSiCl_3$, 0.01 g of H_2PtCl_6 dissolved in 0.5 mL of 2-propanol, 5 h at reflux. (c) Distillation of excess $HSiCl_3$, 20 mL of 1:1 $CH_3CH_2OH–(CH_3CH_2)_3N$, concentration in vacuo, flash chromatography on silica using 1:1 hexane–CH_2Cl_2 eluent. (d) 5 g of 5-μm silica, 0.05 torr, 110 °C, 14 h.

We now describe a broadly applicable CSP derived from (*S*)-(−)-*N*-(2-naphthyl)valine which, owing to its performance and ease of preparation, will almost certainly see early commercialization.[12]

(*S*)-(−)-*N*-(2-Naphthyl)valine **1**, prepared from L-valine and β-naphthol using a variation of the Bucherer reaction,[8] was esterified with 10-undecen-1-ol in the presence of an acid catalyst. Ester **2** was hydrosilylated with trichlorosilane–chloroplatinic acid to afford the chiral trichlorosilane which was converted, without purification, to the less reactive triethoxysilane **3**, by the action of ethanol–triethylamine. This silane was purified by flash chromatography on silica, fully characterized, and bonded to dried 5-μm Spherisorb silica by heating in a Kugelrohr apparatus under vacuum at 110 °C for 14 h. This sequence is shown in Scheme I. Elemental analysis of washed and dried CSP **4** indicates that a loading of 0.3 mmol/g (based on C and N analysis) was achieved. The material was slurry-packed (methanol) into a 4.6 mm × 250 mm stainless steel column.

Table I provides data pertinent to the chromatographic separation of the enantiomers of a representative assortment of analyte classes. In each instance, the analyte has been derivatized with either 3,5-dinitrobenzoyl chloride or 3,5-dinitrophenyl isocyanate. Derivatization incorporates functionality essential to chiral recognition and facilitates detection.

One notes separability factors (e.g., 17.7, 18.7) larger than any yet reported for enantiomer separation for amide derivatives of *N*-(3,5-dinitrobenzoyl)-α-amino acids regardless of whether a simple amine or another amino acid is used in making the amide derivative. Perusal of Table I shows examples of enantiomer separation of the derivatives of secondary and tertiary alcohols,

(1) Pirkle, W. H.; Hyun, M. H.; Bank, B. *J. Chromatogr.* **1984**, *316*, 585–604.
(2) Pirkle, W. H.; Pochapsky, T. C.; Mahler, G. S.; Field, R. M. *J. Chromatogr.* **1985**, *348*, 89–96.
(3) Pirkle, W. H.; Welch, C. J. *J. Org. Chem.* **1984**, *49*, 138–140.
(4) The separability factor is the ratio of retention times measured from the time of elution of a nonretained solute. This ratio is related to the difference in energy of the diastereomeric adsorbates formed when the enantiomers interact with the CSP.
(5) Pirkle, W. H.; House, D. W.; Finn, J. M. *J. Chromatogr.* **1980**, *192*, 143–158.
(6) Ōi, N.; Nagase, M.; Doi, T. *J. Chromatogr.* **1983**, *265*, 111.
(7) Pirkle, W. H.; Mahler, G. S.; Hyun, M. H. *J. Liq. Chromatogr.*, in press.
(8) Pirkle, W. H.; Pochapsky, T. C. *J. Org. Chem.*, in press.
(9) The capacity ratio, k_1', is the number of void volumes of mobile phase beyond the initial void volume needed to elute the first enantiomer.
(10) The resolution, R_S, of the two enantiomers is a measure of the chromatographic efficiency of the separation. An $R_S \geq 1$ indicates effectively complete band separation. R_S is defined by the equation

$$R_S = 2(t_2' - t_1')/(w_2 + w_1)$$

where the t_i's are the corrected retention times of the enantiomers, and the w_i are the widths of the peaks at their bases.
(11) The absolute configuration of the most-retained enantiomer is determined from chromatography of samples enriched in one enantiomer of known configuration.
(12) Note Added in Proof: Columns of this type, derived from valine and from alanine are available in (*R*), (*S*), and (*RS*) forms from Regis Chemical Co., 8210 Austin Av., Morton Grove, IL 60053.