Karen M. Waltz and John F. Hartwig*

Simple transition-metal complexes of the formula $Cp^*M(CO)_n BR_2$ [$Cp^* = C_5(CH_3)_5$] containing an electrophilic, covalently bound main-group ligand react with alkanes and release products resulting from selective functionalization of an alkane at the terminal position. These reactions produce alkylboronate esters, which are common reagents in organic synthesis. Thus, the boryl complexes are rare chemical reagents that react selectivity at the terminal position of an alkane to provide simple functionalized products. Mechanistic analysis shows that ligand dissociation is induced photochemically and that thermal reaction of the resulting intermediate occurs with alkanes.

One major goal of transition-metal chemistry has been the selective functionalization of alkanes (1). Three primary approaches involving transition metals have been followed to achieve this goal: C-H oxidative addition (2), electrophilic cleavage of C-H bonds (3), and oxidation (4). None of these approaches has provided a single isomer of a useful organic product from an alkane. Systems that cleave C-H bonds by oxidative addition or σ -bond metathesis only rarely provide unligated functionalized products (5), and oxidation chemistry has not been selective for a single site of an alkane that contains more than one type of C-H bond. Approaches that do not involve transition metals have centered on radicals or superacids that show selectivity for C–H bonds that is tertiary > secondary > primary (6). The large number of secondary positions in a linear alkane leads to several reaction products.

Here we report a strategy for selective alkane functionalization by transition metals and reveal a reagent for the conversion of alkanes to functionalized products with high selectivity. This reagent is a transition-metal complex that contains an electropositive main-group element bound to the metal. Specifically, the photochemical reaction of $Cp*Fe(CO)_2Bcat'$ [Cp* = $C_5(CH_3)_5$, cat' = 1,2- $O_2\tilde{C_6}H_2$ -3,5- $(\tilde{C}H_3)_2$] $Cp*Ru(CO)_2Bcat'$ (2), (1),and $Cp^*W(CO)_3Bcat'$ (3) with a series of alkanes gives alkylboronate esters with functionalization of the alkane exclusively at the terminal position and in high yields for tungsten complex 3. Little alkane activation chemistry of any type has been observed for tungsten previously (7), and none has been observed for $CpFe(CO)_2R$ (Cp = C_5H_5) and $CpRu(CO)_2R$ complexes. The organoborane products of the chemistry reported here are well-known, highly versatile synthetic intermediates in organic chemistry. Furthermore, the borylation of alkanes could ultimately be developed into a catalytic process, because a number of alkane borylation reactions are either thermoneutral or thermodynamically downhill, depending on the borane (8).

We previously reported the functionalization of arenes by the simple boryl complex CpFe(CO)₂Bcat (cat = $O_2C_6H_4$) (9). However, CpFe(CO)₂Bcat does not react with alkanes, presumably because of reaction of the complex with the sp²-hybridized positions of another CpFe(CO)₂Bcat. Thus, we prepared a derivative of this complex with the sp^2 -hybridized positions blocked. The $Cp*Fe(CO)_2Bcat'$ (1) complex was prepared in 41% yield as yellow crystalline material by the reaction of ClBcat' (10) with a suspension of $Na[Cp*Fe(CO)_2]$ (11) (Eq. 1) in pentane solvent. All metal boryl complexes in this work were isolated in pure form and were fully characterized (12).

[Cp*M(CO) _n]⁺+ ClBcat' → Cp*M(CO) _n Bcat'	(1)
M = Fe, n = 2 (1)	
M = Ru, n = 2 (2)	
M = W, n = 3 (3)	

Irradiation of 1 in neat pentane solvent with a 450-W, medium-pressure Hanovia mercury arc lamp resulted in the formation of a single alkylboronate ester (Eq. 2) in 28% yield, resulting from selective reaction at the terminal position of pentane, as determined by ¹H and ¹¹B nuclear magnetic resonance (NMR) spectroscopy (13), along with gas chromatography (GC)-mass spectroscopy (MS), which showed a clear molecular ion peak. Independent synthesis of the product by hydroboration of 1-pentene with HBcat' (14) and comparison of spectral data and GC retention times confirmed the identity of the product.



The analogous ruthenium boryl compound Cp*Ru(CO)₂Bcat' (2) was prepared in 40% yield by a similar procedure (15). This complex also functionalized pentane (Eq. 2) selectively. The yield of 1-pentylboronate ester was 40% in this case, significantly greater than that for 1. Small (<5% yield) but observable amounts of HBcat' were formed in this reaction.

To determine whether the Cp* and Bcat' groups in 1 and 2 led to alkane functionalization by blocking arene activation or by perturbing the electronic properties of the ligand set, we studied the chemistry of Cp*Fe(CO)₂Bcat and CpFe(CO)₂B[1,2-O₂C₆H₂-3,5-(t-Bu)₂] (Bu = C₄H₉). Neither of these complexes gave substantial amounts of alkane activation products. Thus, the elimination of all accessible sp^2 positions on the metal boryl complex does account for the unusual reactivity.

Because the yields increased for reactions of the second-row, rather than firstrow, metal, we sought a similar, readily accessible boryl complex of a third-row metal. We prepared $Cp*W(CO)_3Bcat'$ (3) from Na[$Cp*W(CO)_3$] (16) and ClBcat' in 67% yield by procedures analogous to those used to prepare 1 and 2. The alkane functionalization chemistry of 3 (Scheme 1) resulted in remarkably high yields.



Complex 3 showed high selectivity for functionalization of alkanes at the primary position, as did 1 and 2. Reaction with pentane gave 1-pentylboronate ester as the only functionalization product in 85% yield. Reaction with ethylcyclohexane gave (2-cyclohexyl)-1-ethylboronate ester as the only functionalization product in 74% yield. Even selectivity for the two terminal positions of isopentane was good. Functionalization of the less hindered position occurred in 55% yield, whereas functionalization at the more hindered terminal position occurred in only 2% yield. We confirmed the absence of products from internal activation in all of the reactions by independently synthesizing the products and noting their absence in the reaction mixtures with the use of GC techniques.

The initial metal-containing products are the metal hydrides $Cp*M(CO)_nH$.

www.sciencemag.org • SCIENCE • VOL. 277 • 11 JULY 1997

Department of Chemistry, Yale University, New Haven, CT 06520-8107, USA.

During the course of the reactions, $Cp*Ru(CO)_2H$ and $Cp*W(CO)_3H$ were observed by ¹H NMR spectroscopy (16, 17). However, $[Cp*M(CO)_n]_2$ complexes (18) were the ultimate metal products as a result of the instability of the metal hydrides to the photochemical conditions).

The primary versus secondary selectivity is highlighted by reaction of 1, 2, and 3 with cyclohexane. Reaction of cyclohexane with the tungsten boryl 3 occurred in only 22% yield; reaction with ruthenium boryl 2 gave only trace amounts of cyclohexylboronate ester; and reaction of cyclohexane with iron boryl 1 gave no products from cyclohexane activation. Thus, all three boryl complexes are much less reactive toward secondary C–H bonds than toward primary C–H bonds.

Preliminary mechanistic studies were performed to determine whether photochemical generation of a boryl radical or photoinduced CO extrusion precedes the alkane activation step. We measured the kinetic isotope effects for compounds 1, 2, and 3 by irradiating the complexes in an equimolar mixture of pentane and pentane d_{12} and analyzing the products by GC-MS. All three metal-boryl systems showed a significant primary isotope effect, but the values were different for each system: 1.9, 2.2, and 5.1 for 1, 2, and 3, respectively. The different values reflect a selectivity for pentane versus pentane- d_{12} and rule out reaction of the same intermediate, such as a boryl radical, with free alkane solvent (19).

These reactions of 1, 2, and 3 with a 1:1 ratio of pentane and pentane- d_{12} also eliminate a potential mechanism involving alkane dehydrogenation and subsequent anti-Markovnikov hydroboration of the resulting alkene. Reaction between 1, 2, or 3 and a 1:1 mixture of pentane and pentane- d_{12} did not produce the d_1 or d_{10} products that would result from such a pathway. Moreover, irradiation of these boryl complexes in the presence of alkenes in alkane solvents gave vinylboronate rather than alkylboronate esters as the dominant products.

Potential pathways for alkane activation by intact boryl complexes (Scheme 2) in-



clude direct reaction of **3** or one of its photochemically excited states with alkane (path A) or initial dissociation of CO followed by thermal reactivity of the resulting 16-electron intermediate with the alkane (path B). A series of data support initial, photochemically induced dissociation of CO that is irreversible: (i) No inhibition of the reactions of 3 was observed under 2 atm of CO; (ii) photolysis of 3 under 1 atm of 13 CO in pentane solvent until half of 3 was consumed resulted in no incorporation of ¹³CO into the remaining starting material (20); (iii) reaction in pentane and pentane d_{12} solvents showed conversions at different time points that were indistinguishable, in contrast to the large isotope effect observed in a 1:1 mixture of the two solvents; (iv) photolysis of 3 in the presence of PMe_3 (Me = CH₃) in pentane solvent led to the formation of $Cp^*W(CO)_2(PMe_3)Bcat'$ (4) by replacement of CO (21), along with 1-pentylboronate ester; and (v) reaction of 3 in pentane containing 2 equivalents of PMe₃ gave a 0.3:1 ratio of 4:pentylboronate ester products after roughly half of the starting complex had been consumed, whereas reaction in the presence of 4 equivalents of PMe_3 produced a 0.6:1 ratio of the two products.

Given the different ratios of products observed during reactions with different concentrations of PMe₃, the photochemically generated intermediate is the branch point for formation of $Cp^*W(CO)_2(PMe_3)$ Bcat' and 1-pentylboronate ester. Considering the many ligand substitution reactions that occur by photochemical extrusion of CO(22), it is most likely that this intermediate is Cp*W(CO)₂Bcat', the 16-electron unsaturated intermediate in path B. Further, the alkane functionalization and phosphine coordination that occur after photochemical generation of this intermediate are likely to be thermal reactions. In this case, the alkane functionalization would be driven by formation of a B-C bond, which is 10 to 15 kcal/mol stronger than the original C-H bond (8). The strengths of a metal-hydride and a metal-boryl bond have been shown previously to be similar (23).

One potential mechanism for alkane functionalization by the 16-electron intermediate involves an endothermic oxidative addition of the alkane C-H bond, followed by exothermic reductive elimination of the alkylboronate ester. The endothermicity of the step involving C-H bond cleavage would account for the previously seen absence of products from alkane oxidative addition with these systems (24). A second potential mechanism would involve direct formation of the alkylboronate ester from the unsaturated intermediate by σ -bond metathesis (25). In this case, the electrophilic, rather than more typical nucleophilic, character of the covalent ligand could explain the unusual regiochemistry, and the presence of both an unsaturated metal center and ligand could explain the unusually high reactivity.

REFERENCES AND NOTES

- B. A. Arndtsen, R. G. Bergman, T. A. Mobley, T. H. Peterson, Acc. Chem. Res. 28, 154 (1995); J. A. Davies, P. L. Watson, J. F. Liebman, A. Greenberg, Eds., Selective Hydrocarbon Activation (Wiley-VCH, New York, 1990); C. L. Hill, Activation and Functionalization of Alkanes (Wiley-Interscience, New York, 1989).
- J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, Mill Valley, CA, ed. 2, 1987), pp. 279–354.
- I. P. Rothwell, in Activation and Functionalization of Alkanes, C. L. Hill, Ed. (Wiley-Interscience, New York, 1989), pp. 151–194.
- R. A. Sheldon and J. K. Kochi, Metal Catalyzed Oxidations of Organic Compounds: Mechanistic Principles and Synthetic Methodology Including Biochemical Processes (Academic Press, New York, 1981).
- W. D. Jones, in Selective Hydrocarbon Activation, J. A. Davies, P. L. Watson, A. Greenberg, J. F. Liebman, Eds. (Wiley-VCH, Weinheim, Germany, 1990), pp. 113–148; J. A. Maguire and A. S. Goldman, J. Am. Chem. Soc. 113, 6706 (1991).
- J. March, Advanced Organic Chemistry (Wiley, New York, 1985).
- J. D. Debad, P. Legzdins, S. A. Lumb, R. J. Batchelor, F. W. B. Einstein, *J. Am. Chem. Soc.* **117**, 3288 (1995).
- 8. P. D. Rablen and J. F. Hartwig, *ibid.* **118**, 4648 (1996).
- K. M. Waltz, X. He, C. N. Muhoro, J. F. Hartwig, *ibid.* 117, 11357 (1995).
- The CIBcat' compound was synthesized in pentane from BCl₃ and 3,5-dimethylcatechol, which was prepared by the procedure of D. D. Weller and E. P. Stirchak [*J. Org. Chem.* 48, 4873 (1983)].
- The solid anions used in this chemistry were prepared by Na/Hg (for Fe and W) or K (for Ru) reduction of the dimers and were heated and washed with toluene to remove as much tetrahydrofuran as possible; V. Guerchais and D. Astruc, *Chem. Commun.* 1985, 835 (1985).
- 12. Spectroscopic and analytical data: Cp*Fe(CO)₂Bcat' (1): ¹H NMR ($C_{e}D_{e}$): chemical shift δ 6.89 ppm (s, 1H), 6.51 (s, 1H), 2.34 (s, 3H), 2.15 (s, 3H), 1.58 (s, 15H); ¹³C {¹H} NMR (C_6D_6): δ 216.52, 151.11, 147.99, 131.05, 124.00, 120.82, 110.04, 96.11, 21.69, 15.26, 10.31; ¹¹B NMR (C_6D_6): δ 54; infrared $\begin{array}{l} (\text{IR}) (C_6 D_6); v_{CO} = 1.996 \text{ cm}^{-1} \text{ (s)}, 1339 \text{ (s)}; \text{ analysis} \\ \text{calculated for } C_{20} H_{23} \text{BO}_4 \text{Fe} \text{ (c)}, 6.096; \text{ H}, 5.88. \\ \text{Found: C, 61.06; H, 5.71. Cp*Ru(CO)}_2 \text{Beat'} \text{ (2): } ^1\text{H} \end{array}$ NMR (C₆D₆): 8 6.90 (s, 1H), 6.52 (s, 1H), 2.35 (s, 3H), 2.15 (s, 3H), 1.71 (s, 15H); ¹³C (¹H) NMR (C_6D_6): δ 203.29, 150.76, 147.64, 131.11, 124.05, 120.89, 110.16, 100.61, 21.70, 15.25, 10.79; ¹¹B NMR $\begin{array}{l} (C_6 D_6): \delta \,48; \, IR \, (C_6 D_6): \nu_{CO} \, 2012 \, (s), \, 1952 \, (s); \, analysis calculated for C_{20} H_{23} BO_4 Ru: C, \, 54.69; \, H, \, 5.28. \\ Found: C, \, 54.77; \, H, \, 5.15. \, CpFe(CO)_2 B[1,2-O_2 C_6 H_2^{-1}] \\ \end{array}$ 3,5- $(t - Bu)_2$]: ¹H NMR (C₆D₆): δ 7.25 (d, J = 1.91 Hz, 1H), 7.16 (d, J = 1.94 Hz, 1H), 4.27 (s, 5H), 1.58 (s, 9H), 1.31 (s, 9H); ¹³C {¹H} NMR (C₆D₆): δ 214.55, 151.31, 146.87, 145.16, 134.00, 115.71, 107.53, 84.22, 35.39, 35.03, 32.41, 30.36; ¹¹B NMR (C₆D₆): $\begin{array}{l} \text{51; } \text{IR} (\text{pentane): } \nu_{\text{CO}} \text{2022 (s), } \text{1969 (s); analysis calculated for } C_{2}\text{H}_{26}\text{BO}_{4}\text{Fe: C, } \text{61.81; H, } \text{6.17.} \\ \text{Found: C, } \text{61.85; H, } \text{6.12. } \text{Cp*Fe(CO)}_2\text{B}(1,2\text{-}) \end{array}$ $\begin{array}{c} \text{Org} C_{\text{B}} \\ \text{2} \\ \text{2} \\ \text{2} \\ \text{1}, 1.55 \ (\text{s}, 15\text{H}); \ ^{19}\text{C} \\ \text{1}^{10}\text{C} \\ \text{1}^{10}\text{C} \\ \text{1}^{11}\text{H} \\ \text{NMR} \ (C_{\text{B}} \\ \text{C}_{\text{B}}): \ \text{3} \\ \text{2} \\ \text{1} \\ \text{1} \\ \text{1} \\ \text{3} \\ \text{1} \\ \text{2} \\ \text{1} \\ \text{3} \\ \text{1} \\ \text{2} \\ \text{1} \\ \text{3} \\ \text{3} \\ \text{1} \\ \text{2} \\ \text{1} \\ \text{$ $\begin{array}{l} (\text{C}_{6}\text{D}_{6}): \delta \; 54; \; \text{IR} \; (\text{pentane}): \; \nu_{CO} \; 1996 \; (\text{s}), \; 1940 \; (\text{s}); \\ \text{analysis calculated for } \text{C}_{18}\text{H}_{,9}\text{BO}_{4}\text{Fe: C}, \; 59.07; \; \text{H}, \\ \text{5.23. Found: C, } 59.08; \; \text{H}, \; 5.23. \; \text{Cp}^{*}\text{W(CO)}_{3}\text{Bcat'} \; \textbf{(3)}: \end{array}$ ¹H NMR (C_6D_6): δ 6.83 (s, 1H), 6.49 (s, 1H), 2.30 (s, 3H), 2.13 (s, 3H), 1.82 (s, 15H); ¹³C {¹H} NMR (C_6D_6): δ 224.07, 219.67, 151.45, 148.48, 131.57, 124.19, 121.16, 110.29, 104.65, 21.63, 15.17, 11.17; ¹¹B NMR (pentane): δ 53; IR (C₆H₆): ν_{CO} 2002 (m), 1920 (s), 1900 (vs); analysis calculated for C₂₁H₂₃BO₅W:

C, 45.81; H, 4.21. Found: C, 45.69; H, 4.17. trans-Cp*W(CO)₂(PMe₃)Bcat' (4): ¹H NMR (C₆D₆): δ 6.90 (s, 1H), 6.52 (s, 1H), 2.40 (s, 3H), 2.15 (s, 3H), 1.92 (s, 15H), 1.29 (d, J_{HP} = 8.9 Hz, 9H); ¹³C {¹H} NMR (C₆D₆): δ 229.63 (d, ²J_{CP} = 19.7 Hz, ¹J_{CW} = 143.0 Hz), 152.03, 149.03, 130.43, 123.37, 122.23, 109.96, 102.65, 21.74, 20.35 (d, J_{CP} = 33.0 Hz), 15.42, 11.79; ¹¹B NMR (C₆D₆): δ 58; ³¹P {¹H} NMR (C₆D₆): δ = 10.6 (s, J_{PW} = 273.4 Hz); IR (C₆D₆): ν_{CO} 1906 (m), 1823 (s); analysis calculated for C₂₃H₃₂BO₄PW: C, 46.19; H, 5.39. Found: C, 46.30; H, 5.39.

- H. Nöth and B. Wrackmeyer, in *NMR Basic Principles and Progress*, P. Diehl, E. Fluck, R. Kosfeld, Eds. (Springer-Verlag, New York, 1978), vol. 14, p. 271.
- 14. The HBcat' compound was synthesized from BH_3 ·Me₂S and 3,5-dimethylcatechol in ether.
- V. Guerchais, C. Lapinte, J.-Y. Thepot, Organometallics 7, 604 (1988).
- A. Stasunik, D. R. Wilson, W. Malisch, J. Organomet. Chem. 270, C18 (1984).
- 17. R. J. Kazlauskas and M. S. Wrighton, *J. Am. Chem.* Soc. **104**, 6005 (1982).
- D. Catheline and D. Astruc, Organometallics 3, 1094 (1984); R. B. King, M. Z. Iqbal, A. D. King, J. Organomet. Chem. 171, 53 (1979); G. O. Nelson and C. E. Sumner, Organometallics 5, 1983 (1986).
- 19. It is possible that a free boryl radical is reacting with a metal-bound alkane. This mechanism would involve both photochemical dissociation of CO to form a

16-electron complex, which would then bind alkane, and photochemical generation of free boryl radical, which would react with the alkane complex. Although this mechanism is consistent with our data, we suggest two simpler mechanisms.

- 20. We showed that ¹³CO was incorporated into the transition metal products, [Cp*W(CO)₃]₂ and Cp^{*}W(CO)₃H, as determined by ¹³C NMR spectroscopy. However, control reactions showed that ¹³CO was incorporated into the products under reaction conditions similar to those of the functionalization process.
- This complex was independently synthesized by reaction of the known Li[Cp*W(CO)₂PMe₃] [S. Schmitzer *et al., Inorg. Chem.* **32**, 303 (1993)] with ClBcat'. Spectral and analytical data are provided in (*12*).
- 22. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1988), vol. 5.
- 23. P. R. Rablen, J. F. Hartwig, S. P. Nolan, J. Am. Chem. Soc. **116**, 4121 (1994).
- The following references describe alkyl hydride products obtained by C–H activation in related metal complexes: J. K. Hoyano, A. D. McMaster, W. A. G. Graham, *ibid.* **105**, 7190 (1983); A. H. Janowicz and R. G. Bergman, *ibid.*, p. 3929; R. G. Bergman, P. F. Seidler, T. T. Wenzel, *ibid.* **107**, 4358 (1985).
 M. E. Thompson *et al.*, *ibid.* **109**, 203 (1987).

4 April 1997; accepted 20 May 1997

Element-Specific Magnetic Anisotropy Determined by Transverse Magnetic Circular X-ray Dichroism

H. A. Dürr, G. Y. Guo, G. van der Laan, J. Lee, G. Lauhoff, J. A. C. Bland

Understanding of the magnetocrystalline anisotropy in magnetic materials (the influence of different elemental components on the direction of easy magnetization) can be greatly enhanced by measuring the orbital moment anisotropy of the elemental constituents. A circular x-ray dichroism technique is presented that allows the determination of the microscopic origin of the spin reorientation transition in ultrathin single-crystalline cobalt/ nickel films. The stronger anisotropy contribution of a much thinner cobalt layer redirects the easy magnetization direction of the entire film.

Understanding of the magnetic anisotropy in nanostructures is of both scientific and technological importance. In device applications, such as magnetic and magnetooptic recording, the use of different magnetic materials such as alloys or layered systems allows tailoring of the magnetic anisotropy, that is, the easy direction of magnetization. So far it has only been possible to measure the magnetic anisotropy of the total system. We report here the separate measurement of the anisotropy contributions of the elemental constituents with transverse magnetic circular x-ray dichroism (TMCXD). The difference in x-ray absorption between left and right circularly polarized light is measured in a transverse geometry where for an isotropic sample the dichroism signal vanishes.

We studied the changes in the magnetocrystalline anisotropy (MCA) that occurred when an ultrathin Co film was deposited onto a 33-monolaver-(ML)-thick Ni layer. The films were grown and structurally characterized under ultrahigh vacuum conditions as described in detail elsewhere (1). The conventional way to obtain information about magnetic anisotropies is through hysteresis loops (Fig. 1). In the 33-ML Ni film, the spins are remanently oriented along the sample normal. Deposition of only 3 ML of Co onto the Ni surface forces the spins into the surface plane. With the magneto-optical Kerr effect, which is the usual method to measure the loops in Fig. 1, it is not possible to distinguish between the different elements Co and Ni (2). Magnetometry with conventional MCXD can in principle achieve this by measuring the elementresolved orientation of the spin magnetic moments (3). However, because of the strong exchange coupling between Ni and Co, the hysteresis loops for the two elements are identical, making it difficult to differentiate between the different mechanisms describing the behavior displayed in Fig. 1. It has been shown that the perpendicular magnetic anisotropy of the Ni film in Fig. 1 is related to the Ni in-plane lattice expansion in the epitaxial Ni/Cu system (1, 4). Thus, the Co top layer, which favors a smaller lattice parameter than the substrate (5), could be forcing the spins in-plane through a strain reduction in the Ni layer. An alternative is that face-centered-cubic Ni and Co lattices respond differently to strain; Ni has an easy magnetization axis perpendicular to the direction of the lattice expansion, whereas the Co spins prefer to be parallel (6). We show below the close relation between MCA and the orbital moment anisotropy. Element-specific TMCXD measurements show that it is indeed the stronger in-plane anisotropy of the thinner Co layer that forces the larger magnetic moment of the Ni layer in-plane.

The leading contribution to the MCA is thought to be the spin-orbit coupling (7, 8). It can be shown that, for 3*d* transition metal magnets, the spin-orbit contribution to the ground-state energy *E* is proportional to the scalar product of the expectation value of the orbital moment vector **L** and a unit vector **S** in the direction of the sample magnetization (9)

$$E \propto -\xi \mathbf{L} \cdot \mathbf{S} \tag{1}$$

where ξ is the spin-orbit coupling parameter. This result is very intuitive. It shows that the spin-orbit coupling tries to align L and S (anti)parallel to each other to minimize the total energy of the system. The negative sign applies to the transition metals with more than half-filled 3d shells and corresponds to a parallel alignment of L and S. In transition metals, the orbital moment is determined by the interplay of the spinorbit coupling with the much stronger crystalline field interaction. It is the crystalline field that acts directly on the electron orbits and fixes L relative to the crystal lattice. As a consequence, we obtain different values of L if the spins are oriented along different crystal directions by a strong external magnetic field. The easy magnetization direction N is then given as the direction with the largest component of L that results in the lowest energy (Eq. 1). This important relation of the orbital moment and the MCA has recently been verified experimentally by Weller *et al.* (10).

L and S are parallel when S is along a high-symmetry direction of the crystalline

REPORTS

H. A. Dürr, G. Y. Guo, G. van der Laan, Daresbury Laboratory, Warrington WA4 4AD, UK. J. Lee, G. Lauhoff, J. A. C. Bland, Cavendish Laboratory,

University of Cambridge, Cambridge CB3 0HE, UK.