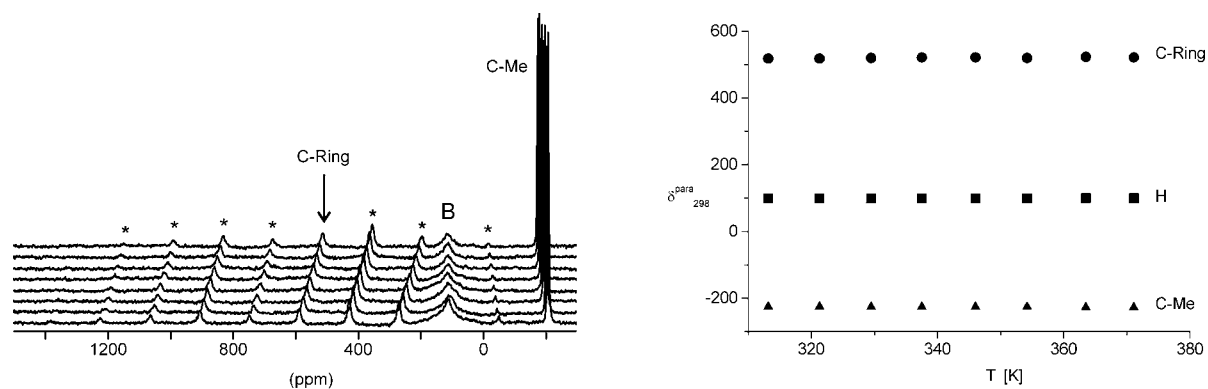


Inter- and Intramolecular Spin Transfer in Molecular Magnetic  
Materials. Solid-State NMR Spectroscopy of Paramagnetic  
Metallocenium Ions

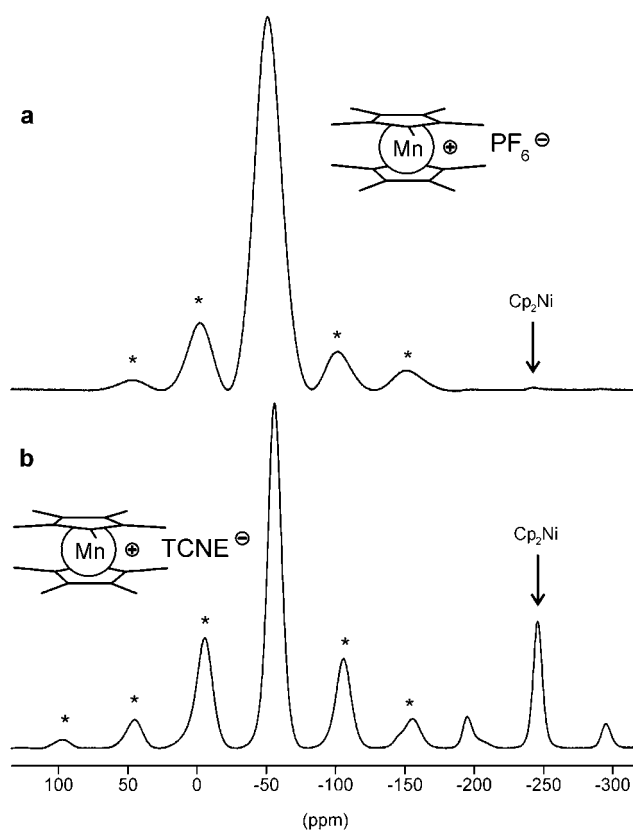
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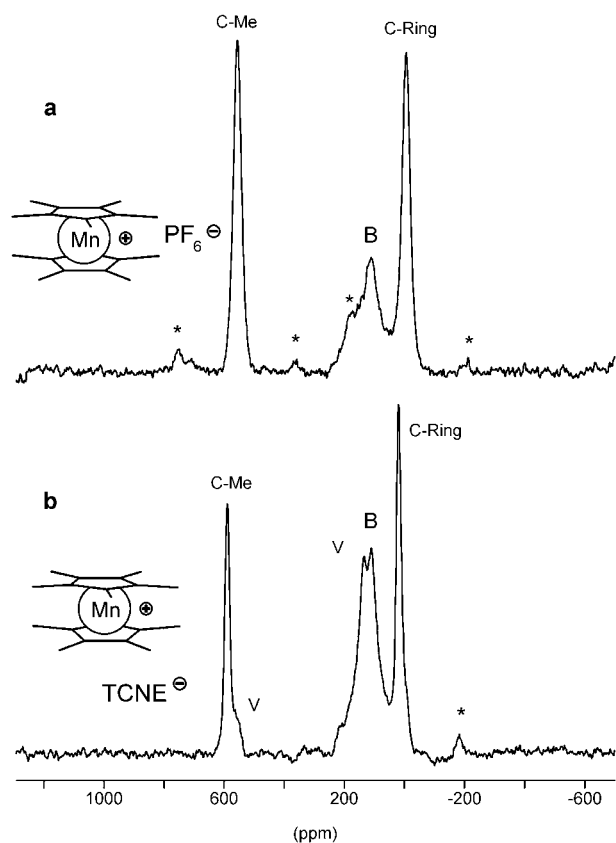
**SUPPORTING INFORMATION**



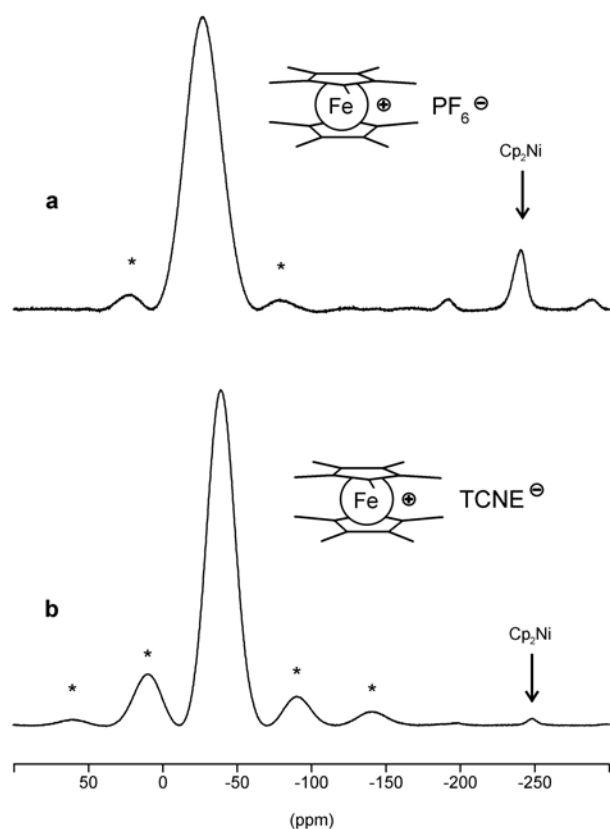
**Figure SI1.** Left:  $^{13}\text{C}$  MAS NMR spectra of  $[(\text{C}_5\text{Me}_5)_2\text{Ni}]^+ [\text{PF}_6]^-$  at 363.5, 354.2, 346.0, 337.5, 329.5, 321.3, 313.2, and 296.3 K (top to bottom). Spinning rate 12 kHz, B = background signal of the probehead, spinning sidebands are marked by asterisks. Right: Reduced paramagnetic shifts  $\delta_{298}^{\text{para}}$  of the  $^{13}\text{C}$  and  $^1\text{H}$  MAS NMR signals of  $[(\text{C}_5\text{Me}_5)_2\text{Ni}]^+ [\text{PF}_6]^-$  as a function of the temperature (see above).



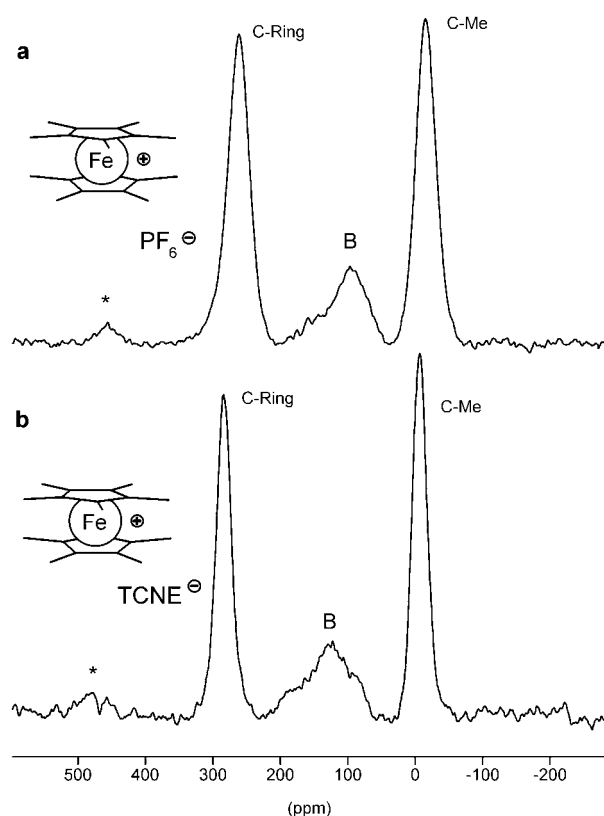
**Figure SI2.**  $^1\text{H}$  MAS NMR spectra of  $[(\text{C}_5\text{Me}_5)_2\text{Mn}]^+ [\text{PF}_6]^-$  at 311.0 K and 14.5 kHz (a) and of  $[(\text{C}_5\text{Me}_5)_2\text{Mn}]^+ [\text{TCNE}]^-$  at 307.0 K 15.0 kHz (b).  $\text{Cp}_2\text{Ni}$  is the internal temperature standard, spinning sidebands are marked by asterisks.



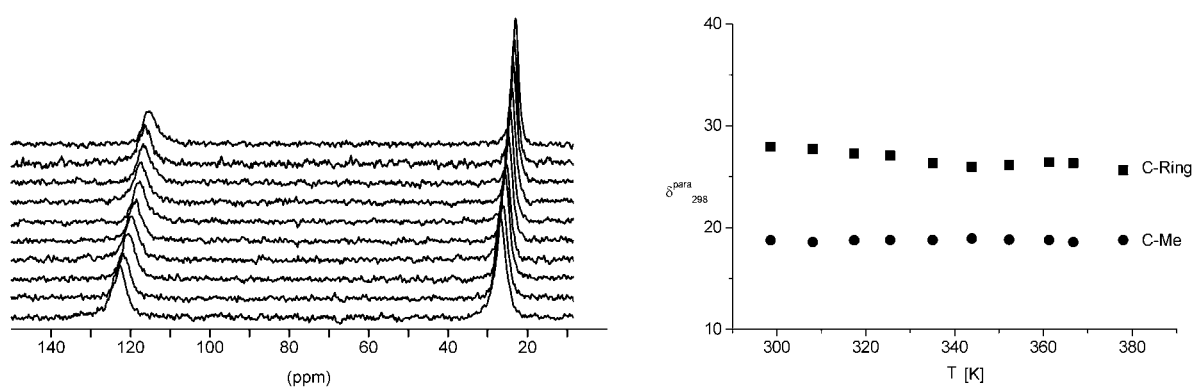
**Figure SI3.**  $^{13}\text{C}$  MAS NMR spectra of  $[(\text{C}_5\text{Me}_5)_2\text{Mn}]^+ [\text{PF}_6]^-$  at 311.0 K and 14.5 kHz (a) and of  $[(\text{C}_5\text{Me}_5)_2\text{Mn}]^+ [\text{TCNE}]^-$  at 307.0 K 15.0 kHz (b). B = background signal of the probehead, V = impurities, spinning sidebands are marked by asterisks.



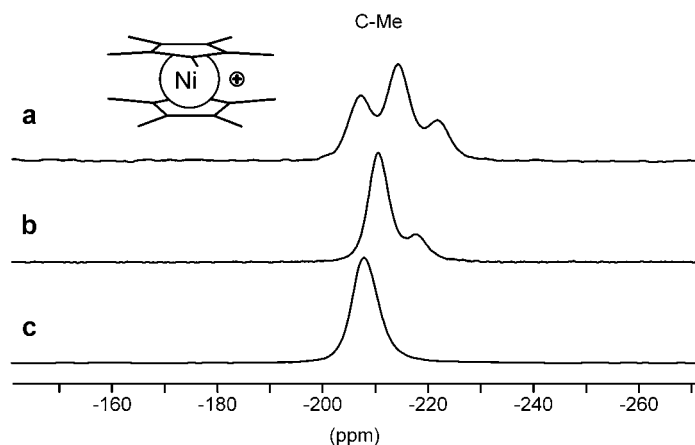
**Figure SI4.**  $^1\text{H}$  MAS NMR spectra of  $[(\text{C}_5\text{Me}_5)_2\text{Fe}]^+ [\text{PF}_6]^-$  at 313.7 K and 14.5 kHz (a) and of  $[(\text{C}_5\text{Me}_5)_2\text{Fe}]^+ [\text{TCNE}]^-$  at 304.5 K 15.0 kHz (b).  $\text{Cp}_2\text{Ni}$  is the internal temperature standard, spinning sidebands are marked by asterisks.



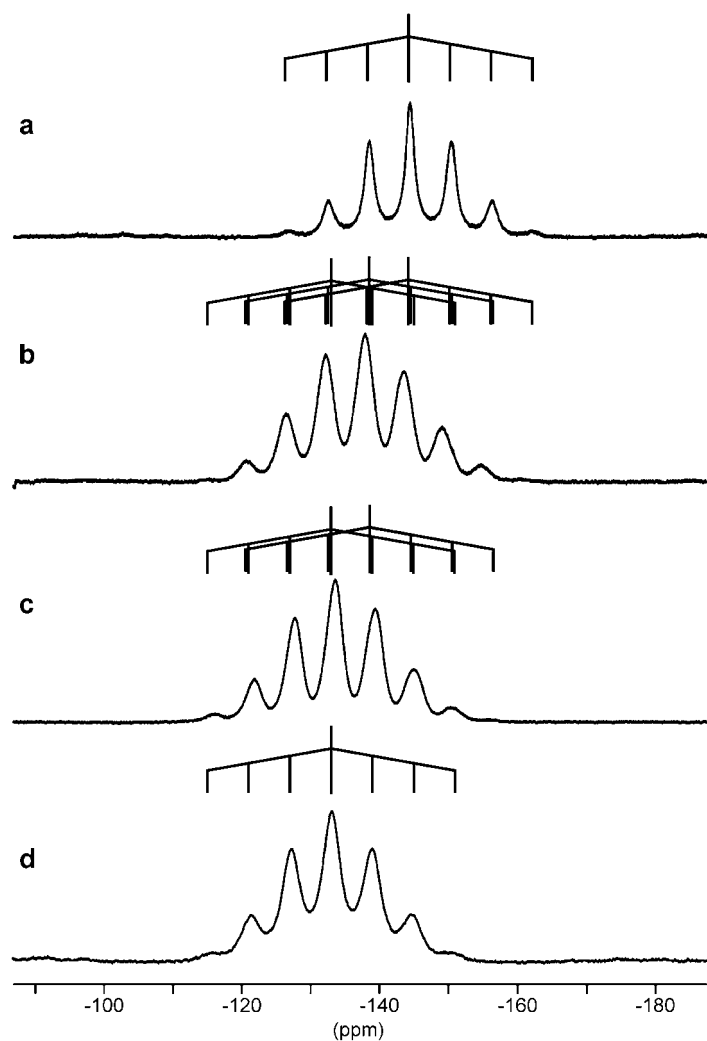
**Figure S15.**  $^{13}\text{C}$  MAS NMR spectra of  $[(\text{C}_5\text{Me}_5)_2\text{Fe}]^+ [\text{PF}_6]^-$  at 313.7 K and 14.5 kHz (a) and of  $[(\text{C}_5\text{Me}_5)_2\text{Fe}]^+ [\text{TCNE}]^-$  at 304.5 K 15.0 kHz (b). B = background signal of the probehead, spinning sidebands are marked by asterisks.



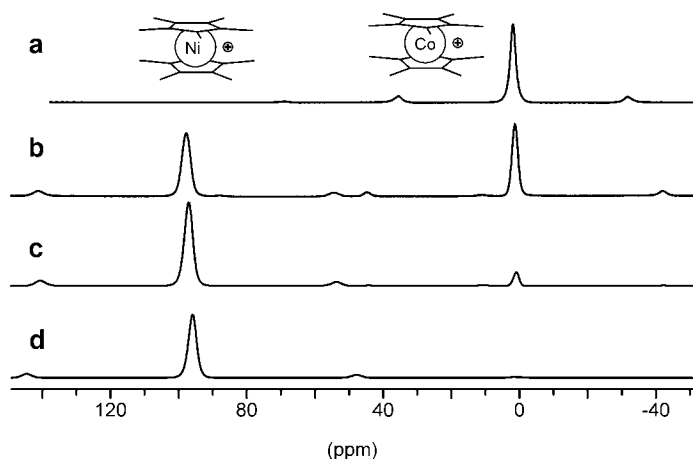
**Figure S16.** Left:  $^{13}\text{C}$  MAS NMR spectra of  $[(\text{C}_5\text{Me}_5)_2\text{Co}]^+ [\text{TCNE}]^-$  at 378.0, 366.7, 361.3, 352.3, 343.9, 335.1, 325.5, 317.4, 308.1, and 298.6 K (top to bottom). Spinning rate 8 kHz. Right: Reduced paramagnetic shifts  $\delta_{298}^{\text{para}}$  of the  $^{13}\text{C}$  MAS NMR signals of  $[(\text{C}_5\text{Me}_5)_2\text{Co}]^+ [\text{TCNE}]^-$  as a function of the temperature (see above).



**Figure SI7.**  $^{13}\text{C}$  MAS NMR spectra of the  $[(\text{C}_5\text{Me}_5)_2\text{Ni}]^+$  cation in the mixed crystals  $[(\text{C}_5\text{Me}_5)_2\text{Ni}_x\text{Co}_{1-x}]^+ [\text{PF}_6]^-$  for  $x = 0.6$  (a),  $0.9$  (b), and  $1.0$  (c). Spinning rates  $15\text{ kHz}$  (a),  $13\text{ kHz}$  (b), and  $14.5\text{ kHz}$  (c); temperatures  $313\text{ K}$  (a),  $308\text{ K}$  (b), and  $310.5\text{ K}$  (c).



**Figure SI8.**  $^{31}\text{P}$  MAS NMR spectra of the mixed crystals  $[(\text{C}_5\text{Me}_5)_2\text{Ni}_x\text{Co}_{1-x}]^+ [\text{PF}_6]^-$  for  $x = 0$  (a),  $0.6$  (b),  $0.9$  (c), and  $1.0$  (d). Spinning rates were  $5.0\text{ kHz}$  (a and d),  $7.0\text{ kHz}$  (b), and  $12.0\text{ kHz}$  (c).



**Figure SI9.**  $^1\text{H}$  MAS NMR spectra of the mixed crystals  $[(\text{C}_5\text{Me}_5)_2\text{Ni}_x\text{Co}_{1-x}]^+ [\text{PF}_6]^-$  for  $x = 0$  (a), 0.6 (b), 0.9 (c), and 1.0 (d). Temperatures: 308.0 K (b and c) and 313.5 K (d) Spinning rates: 10.0 kHz (a), 13.0 kHz (b and c), and 14.5 kHz (d).

### Crystal Structure of $[(\text{C}_5\text{Me}_5)_2\text{Co}]^+ [\text{PF}_6]^-$ , Details Relevant for Dipolar NMR Signal Shifts

**Table SI1.** Crystal Data and Structure Refinement of  $[(\text{C}_5\text{Me}_5)_2\text{Co}]^+ [\text{PF}_6]^-$  (extended version)

|                                      |                                                    |
|--------------------------------------|----------------------------------------------------|
| chemical formula                     | $[\text{CoC}_{20}\text{H}_{30}]^+ [\text{PF}_6]^-$ |
| formula weight                       | 474.36                                             |
| crystal system                       | monoclinic                                         |
| space group                          | C2/m                                               |
| color of crystal                     | yellow                                             |
| dimensions of crystal                | 0.5 · 0.45 · 0.25 mm                               |
| unit cell parameters                 |                                                    |
| $a$ (Å)                              | 14.0459(9)                                         |
| $b$ (Å)                              | 8.9028(4)                                          |
| $c$ (Å)                              | 9.1186(5)                                          |
| $\beta$ (deg)                        | 112.724(2)                                         |
| volume (Å <sup>3</sup> )             | 1051.8(1)                                          |
| $Z$                                  | 2                                                  |
| absorption coeff (mm <sup>-1</sup> ) | 0.947                                              |
| max. and min. transmission           | 1.000 and 0.484                                    |
| temperature (K)                      | 199(2)                                             |
| $\lambda$ (Å)                        | 0.7103                                             |
| $\theta$ range (deg.)                | 3 - 27                                             |
| number of data and cut off           | 1197 with $I > 3\sigma(1)$                         |
| number of parameters refined         | 83                                                 |

|                                                                                                                                        |                      |
|----------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| goodness of fit                                                                                                                        | 1.146                |
| density (Mg/m <sup>3</sup> ) (calcd)                                                                                                   | 1.498                |
| intensity measurement method                                                                                                           | $\omega/\theta$ scan |
| R1 <sup>a</sup>                                                                                                                        | 0.0332               |
| wR2 <sup>b</sup>                                                                                                                       | 0.0905               |
| <sup>a</sup> R1 = $\Sigma   F_o  -  F_c   / \Sigma  F_o $ . <sup>b</sup> wR2 = $(\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o ^2)^{1/2}$ . |                      |

**Table SI2.** Positional ( $\times 10^4$ ) and Thermal Parameters [ $\text{pm}^2 \cdot 10^{-1}$ ]

| Atom    | x/a     | y/b     | z/c      | U(eq) |
|---------|---------|---------|----------|-------|
| Kation: |         |         |          |       |
| Co      | 0       | 0       | 0        | 19(1) |
| C(1)    | 1398(1) | 802(2)  | 1564(2)  | 27(1) |
| C(2)    | 1197(1) | 1300(2) | -20(2)   | 29(1) |
| C(3)    | 1081(2) | 0       | -990(3)  | 30(1) |
| C(4)    | 1631(2) | 1778(3) | 2987(3)  | 51(1) |
| C(5)    | 1137(2) | 2898(3) | -557(3)  | 53(1) |
| C(6)    | 917(3)  | 0       | -2715(4) | 56(1) |
| Anion:  |         |         |          |       |
| P       | 0       | 5000    | 5000     | 28(1) |
| F(1)    | 0       | 3216(2) | 5000     | 63(1) |
| F(2)    | 525(2)  | 5000    | 3728(2)  | 48(1) |
| F(3)    | 1103(2) | 5000    | 6417(2)  | 63(1) |

At 199 K the rotation of the cations about the fivefold symmetry axis and the reorientation of the hexafluorophosphate anions are frozen, so that distinct positions for all carbon and fluorine atoms are resolved. As shown in Figure 10, the cations are all aligned with their fivefold symmetry axes parallel to each other. The metal centers of the sandwich cations occupy the corners of the unit cell and the center of the *ab* planes, the phosphorous atoms of  $[\text{PF}_6]^-$  are located at the centers of the *ac* and the *bc* planes. Each cation has two equivalent nearest neighbor cations along the *b* and *c* directions and four equivalent nearest neighbors in the *ab* plane. Also important for the dipolar signal shifts are the centers of the  $(\text{C}_5\text{Me}_5)$  ligands of  $[(\text{C}_5\text{Me}_5)_2\text{M}]^+$ ; they have only two rather than four nearest neighbor cations in the *ab* plane. As for the anions, each has four equivalent nearest neighbor cations in the corners of the *bc* plane, two along the direction of the short diagonal of the *ac* plane, and two along the direction of the long diagonal of the *ac* plane, somewhat further apart. For the determination of the interionic

dipolar signal shifts the following distances and angles (defined in (Figure SI9) and listed in Table SI3) are needed.

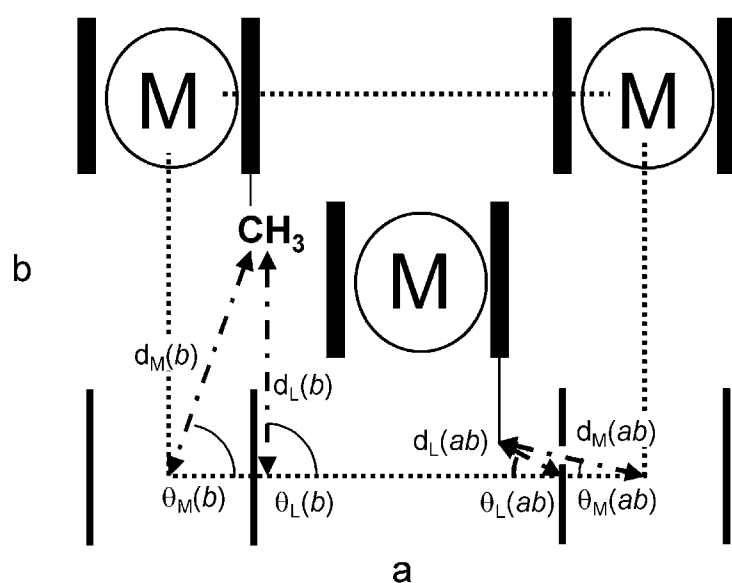
$d_M(b)$  and  $d_M(ab)$ : distances of the methyl carbon atoms of a given ( $C_5Me_5$ ) ligand from the metal centers of the nearest neighbor cations,

$d_L(b)$  and  $d_L(ab)$ : distance of the methyl carbon atoms of a given ( $C_5Me_5$ ) ligand from the centers of the closest ( $C_5Me_5$ ) ligands of the nearest neighbor cations,

$\theta_M(b)$  and  $\theta_M(ab)$ : angle between the distance vector  $d_M$  and the fivefold axis of the nearest neighbor cation,

$\theta_L(b)$  and  $\theta_L(ab)$ : angle between the distance vector  $d_L$  and the fivefold axis of the nearest neighbor cation.

The corresponding distances and angles that the phosphorus atom of  $[PF_6]^-$  has with the neighboring cations 1 and 2 are given as primed entries in Table SI3.



**Figure SI9.** Projection of the cations of  $[(C_5Me_5)_2Co]^+ [PF_6]^-$  in the  $ab$  plane (not to scale) with interionic distances and angles relevant for dipolar signal shifts.

**Table SI3.** Interionic Distances and Angles of  $[(C_5Me_5)_2Co]^+ [PF_6]^-$  Relevant for Dipolar Signal Shifts

| methyl carbon atoms of (C <sub>5</sub> Me <sub>5</sub> ) |                                      |                                      |                                      |                                       |                                       |                                       |                                       |                                       |                                       |
|----------------------------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| <i>d</i> <sub>M</sub> ( <i>ab</i> )                      | <i>θ</i> <sub>M</sub> ( <i>ab</i> )  | <i>d</i> <sub>L</sub> ( <i>ab</i> )  | <i>θ</i> <sub>L</sub> ( <i>ab</i> )  | <i>d</i> <sub>M</sub> ( <i>b</i> )    | <i>θ</i> <sub>M</sub> ( <i>b</i> )    | <i>d</i> <sub>L</sub> ( <i>b</i> )    | <i>θ</i> <sub>L</sub> ( <i>b</i> )    |                                       |                                       |
| [Å]                                                      | [°]                                  | [Å]                                  | [°]                                  | [Å]                                   | [°]                                   | [Å]                                   | [°]                                   |                                       |                                       |
| 5.5744                                                   | 20.9                                 | 5.816                                | 126.5                                | 6.589                                 | 104.5                                 | 6.379                                 | 90                                    |                                       |                                       |
| 6.9279                                                   | 42.4                                 | 4.073                                | 150.8                                | 7.838                                 | 102.9                                 | 9.307                                 | 90                                    |                                       |                                       |
| 6.9183                                                   | 41.8                                 | 5.793                                | 127.7                                | 10.853                                | 99.3                                  | 11.513                                | 90                                    |                                       |                                       |
| 8.7755                                                   | 53.6                                 | 7.907                                | 116.7                                | 11.631                                | 98.2                                  | 10.712                                | 90                                    |                                       |                                       |
| 8.728                                                    | 54.1                                 | 7.875                                | 116.1                                | 9.461                                 | 100.4                                 | 7.641                                 | 90                                    |                                       |                                       |
| phosphorus atom of [PF <sub>6</sub> ] <sup>−</sup>       |                                      |                                      |                                      |                                       |                                       |                                       |                                       |                                       |                                       |
| <i>d</i> <sub>M</sub> '( <i>bc</i> )                     | <i>θ</i> <sub>M</sub> '( <i>bc</i> ) | <i>d</i> <sub>L</sub> '( <i>bc</i> ) | <i>θ</i> <sub>L</sub> '( <i>bc</i> ) | <i>d</i> <sub>M</sub> '( <i>ac1</i> ) | <i>θ</i> <sub>M</sub> '( <i>ac1</i> ) | <i>d</i> <sub>L</sub> '( <i>ac1</i> ) | <i>θ</i> <sub>L</sub> '( <i>ac1</i> ) | <i>d</i> <sub>M</sub> '( <i>ac2</i> ) | <i>θ</i> <sub>M</sub> '( <i>ac2</i> ) |
| [Å]                                                      | [°]                                  | [Å]                                  | [°]                                  | [Å]                                   | [°]                                   | [Å]                                   | [°]                                   | [Å]                                   | [°]                                   |
| 6.372                                                    | 90                                   | 6.786                                | 68.786                               | 6.736                                 | 26.3                                  | 5.305                                 | 145.8                                 | 9.73                                  | 37.9                                  |

### Dipolar Signal Shifts

If the electron g tensor is not isotropic, the direction of the mean magnetic moment of the electron spin depends on the orientation of the molecule within the external magnetic field, and the dipolar interaction with the nucleus is not averaged completely to zero under rapid molecular reorientation or magic-angle spinning, but results in the dipolar shift  $\delta^{\text{dip}}$ . For the idealized assumption that the unpaired electron is localized on the metal,  $\delta^{\text{dip}}$  can be calculated according to the point-dipol model:<sup>SI1</sup>

$$\delta^{\text{dip}} = 10^6 \cdot \frac{\mu_0}{4\pi} \cdot \frac{\beta_e^2 S(S+1)}{9kT} \cdot G(d, \theta) \cdot (g_{\parallel}^2 - g_{\perp}^2) \cdot f(g, D) = C \cdot G(d, \theta). \quad (\text{SI1})$$

$\mu_0$  is the magnetic field constant,  $\beta_e$  is the Bohr magneton,  $S$  is the electron spin,  $k$  is the Boltzmann factor,  $T$  is the absolute temperature,  $g_{\parallel}$  and  $g_{\perp}$  are the respective g factors parallel and perpendicular to the magnetic axis,  $f(g, D)$  is a function of the g factor and its rhombicity when  $S > 1/2$ , and  $G(d, \theta)$  is the geometric factor

$$G(d, \theta) = \frac{3 \cos^2 \theta - 1}{d^3}. \quad (\text{SI2})$$

In eq SI2  $d$  is the electron-nucleus distance and  $\theta$  the angle between the symmetry axis of the molecule and the distance vector  $d$ .

We are interested in the interactions between the lattice components of  $[(C_5Me_5)_2M]^+ [PF_6]^-$ . As for the interionic dipolar signal shifts, there are two contributions,  $\delta^{\text{dip}, M}$  and  $\delta^{\text{dip}, L}$ , for any nucleus of  $[(C_5Me_5)_2M]^+ [PF_6]^-$ . They are due to the spin centered on the nearest of the two ligands,  $5 \cdot \rho_p$ , and the metal-centered spin,  $1-10 \cdot \rho_p$ , on the nearest  $[(C_5Me_5)_2M]^+$  cations, respectively. Although  $\rho_p$  is small,  $\delta^{\text{dip}, L}$  must be taken into account, because the distance  $d$  in eq (SI2) is also small. Spin density on more distant cations can be neglected. Therefore, the overall dipolar signal shift is

$$\delta^{\text{dip}} = \delta^{\text{dip}, M} + \delta^{\text{dip}, L} = C \cdot [(1-10 \cdot \rho_p) \langle G(\theta_M, d_M) \rangle + 5 \cdot \rho_p \cdot \langle G(\theta_L, d_L) \rangle]. \quad (\text{SI3})$$

When this is applied to the dipolar  $^{13}\text{C}$  NMR signal shifts of the methyl carbon atoms of the  $[(C_5Me_5)_2M]^+$  cations,  $C$  can be calculated by using eq (SI1), the  $g$  values in Table SI5, and the  $\rho_p$  values in Table 3 (divided by ten for the spin density at one ring carbon atom); for  $[(C_5Me_5)_2Fe]^+ [PF_6]^-$   $\rho_p$  was estimated to be  $-0.1\%$ . The terms  $\langle G(\theta, d_i) \rangle$  are the averaged geometric factors for the methyl carbon atoms. Since only one signal was found for the protons and the chemically different  $^{13}\text{C}$  nuclei of solid  $[(C_5Me_5)_2M]^+ [PF_6]^-$ , the  $(C_5Me_5)$  ligand undergoes rapid  $2\pi/5$  jumps about the symmetry axis, and the average geometric factors can be calculated by

$$\langle G(d_i, \theta_i) \rangle = \frac{1}{5} \cdot \sum_{k=1}^5 \frac{3 \cos^2 \theta_i^k - 1}{(d_i^k)^3}, \quad (\text{SI4})$$

where  $d_i$  and  $\theta_i$  are the distances and angles listed in the upper part of Table SI3. For the dipolar signal shifts from the two nearest neighbor cations in the  $ab$  plane the average geometric factors are  $\langle G(d_M, \theta_M) \rangle = 0.002680 \text{ \AA}^{-3}$  and  $\langle G(d_L, \theta_L) \rangle = 0.003663 \text{ \AA}^{-3}$ , for the two nearest neighbors along the  $b$  axis these factors are  $\langle G(d_M, \theta_M) \rangle = -0.001398 \text{ \AA}^{-3}$  and  $\langle G(d_L, \theta_L) \rangle = -0.001761 \text{ \AA}^{-3}$ . The total intermolecular dipolar shifts due to the dipolar interactions with the four nearest neighbor cations,  $\delta^{\text{dip}}_{\text{total}} = 2 \cdot \delta^{\text{dip}}(ab) + 2 \cdot \delta^{\text{dip}}(b)$  (calculated from eq. (SI3)) are given in Table SI4.

**Table SI4.** Dipolar  $^{13}\text{C}$  NMR shifts of the Methyl Groups of  $[(\text{C}_5\text{Me}_5)_2\text{M}]^+ [\text{PF}_6]^-$  Resulting from Interaction with Nearest Neighbor Cations.

| metal                                | $[(\text{C}_5\text{Me}_5)_2\text{M}]^+ [\text{PF}_6]^-$ |        |
|--------------------------------------|---------------------------------------------------------|--------|
|                                      | Ni                                                      | Cr     |
| $\delta^{\text{dip}}(ab)$            | -0.27                                                   | -0.007 |
| $\delta^{\text{dip}}(b)$             | 0.14                                                    | 0.09   |
| $\delta^{\text{dip}}_{\text{total}}$ | -0.26                                                   | 0.166  |

The same approach is applied to the  $[\text{PF}_6]^-$  anions that experience dipolar  $^{31}\text{P}$  NMR signal shifts from the neighbor cations  $[(\text{C}_5\text{Me}_5)_2\text{M}]^+$ . The geometric factors for the four nearest neighbors in the  $bc$  plane are  $G(d_{\text{M}}, \theta_{\text{M}}) = -0.003865 \text{ \AA}^{-3}$  and  $G(d_{\text{L}}, \theta_{\text{L}}) = -0.001943 \text{ \AA}^{-3}$  (for each  $(\text{C}_5\text{Me}_5)$  ligand), for the two nearest neighbors in the  $ac$  plane they are  $G(d_{\text{M}}, \theta_{\text{M}}) = 0.004617 \text{ \AA}^{-3}$  and  $G(d_{\text{L}}, \theta_{\text{L}}) = 0.007048 \text{ \AA}^{-3}$  (for the nearest  $(\text{C}_5\text{Me}_5)$  ligand), and for the two remote cations in the  $ac$  plane it is  $G(d_{\text{M}}, \theta_{\text{M}}) = 0.000942 \text{ \AA}^{-3}$  (the  $(\text{C}_5\text{Me}_5)$  ligands are far apart, their contributions are neglected). The total intermolecular dipolar shifts due to the dipolar interactions with the eight nearest neighbor cations,  $\delta^{\text{dip}}_{\text{total}} = 4 \cdot \delta^{\text{dip}}(bc) + 2 \cdot \delta^{\text{dip}}(ac1) + 2 \cdot \delta^{\text{dip}}(ac2)$  are given in Table SI5.

**Table SI5.** Dipolar Shifts of the  $^{31}\text{P}$  NMR Signals of  $[(\text{C}_5\text{Me}_5)_2\text{M}]^+ [\text{PF}_6]^-$  Resulting from Interactions with Different Nearest Neighbor Cations

| metal                                | $[(\text{C}_5\text{Me}_5)_2\text{M}]^+ [\text{PF}_6]^-$ |                      |                     |                      |
|--------------------------------------|---------------------------------------------------------|----------------------|---------------------|----------------------|
|                                      | Ni                                                      | Fe                   | Mn                  | Cr                   |
| $\text{C}^{\text{a}}$                | $-1.13 \cdot 10^2$                                      | $3.1 \cdot 10^3$     | $-1.5 \cdot 10^3$   | -68.2                |
| $g_{\parallel}$                      | $1.852^{\text{SI2}}$                                    | $4.433^{\text{SI3}}$ | $2.33^{\text{SI4}}$ | $2.004^{\text{SI5}}$ |
| $g_{\perp}$                          | $2.02^{\text{SI2}}$                                     | $1.35^{\text{SI3}}$  | $2.77^{\text{SI4}}$ | $2.015^{\text{SI5}}$ |
| $\delta^{\text{dip}}(bc)$            | 0.3                                                     | -12.9                | 4.8                 | 0.3                  |
| $\delta^{\text{dip}}(ac1)$           | -0.5                                                    | 14.7                 | -5.5                | -0.3                 |
| $\delta^{\text{dip}}(ac2)$           | -0.1                                                    | 3.2                  | -1.2                | -0.1                 |
| $\delta^{\text{dip}}_{\text{total}}$ | 0.0                                                     | -15.8                | 5.8                 | 0.4                  |

<sup>a</sup> C values (in  $\text{ppm} \cdot \text{\AA}^3$ ) at  $T = 298 \text{ K}$  for the  $[(\text{C}_5\text{Me}_5)_2\text{M}]^+$  cations calculated with eq (SI1).

### Cell parameters for $[(C_5Me_5)_2M]^+ [PF_6]^-$

X-ray powder diffractograms (CuK $\alpha$  radiation) were obtained for the pure hexafluorophosphates  $[(C_5Me_5)_2M]^+ [PF_6]^-$  (M = Ni, Fe, Mn, Cr, and Co) and the mixed crystals  $[(C_5Me_5)_2Ni_xCo_{1-x}]^+ [PF_6]^-$  (x = 0.9 and 0.6), although some were of poor quality. All powder diffractograms showed one set of similar reflection angles, thus proving that these compounds are isostructural.

The plane distances  $d$  obtained from the powder diffractograms were assigned to the different lattice planes by comparison with the theoretical plane distances in  $[(C_5Me_5)_2Co]^+ [PF_6]^-$ . Selected  $d$  values for the different compounds are given in Table SI6. The cell parameters (Table SI7) were obtained from the assigned  $d$  values by least-squares fit to the Bragg-equation.

**Table SI6.**  $d$  Values for Lattice Planes ( $h,k,l$ ) of  $[(C_5Me_5)_2M]^+ [PF_6]^-$  Used for the Determination of the Cell Parameters.

| $[(C_5Me_5)_2M]^+ [PF_6]^-$ |       |      |      |      |                                     |                                     |      |
|-----------------------------|-------|------|------|------|-------------------------------------|-------------------------------------|------|
| M                           | Cr    | Mn   | Fe   | Ni   | Ni <sub>0.6</sub> Co <sub>0.4</sub> | Ni <sub>0.9</sub> Co <sub>0.1</sub> | Co   |
| $h, k, l$                   | $d$   |      |      |      |                                     |                                     |      |
| 0, 0, 1                     |       |      | 8.41 |      | 8.43                                |                                     | 8.41 |
| 1, 1, 1                     | 5.19  | 5.13 | 5.07 | 5.11 | 5.04                                | 5.10                                | 5.01 |
| 1, 1, -1                    | 6.17  | 6.24 | 6.28 | 6.28 | 6.24                                | 6.28                                | 6.25 |
| 2, 0, 0                     | 6.94  | 6.73 | 6.61 | 6.71 | 6.53                                | 6.68                                | 6.48 |
| 2, 0, 1                     | 4.28  | 4.35 | 4.41 | 4.45 | 4.41                                | 4.40                                | 4.38 |
| 0, 0, 2                     | 4.21  | 4.22 | 4.23 | 4.19 | 4.14                                | 4.26                                | 4.21 |
| 0, 2, 0                     | 4.43  | 4.46 | 4.44 | 4.48 | 4.44                                | 4.45                                | 4.45 |
| 2, 2, 0                     | 3.648 | 3.72 | 3.70 | 3.72 | 3.67                                | 3.70                                | 3.67 |

**Table SI7.** Cell Parameters of the Hexafluorophosphates  $[(C_5Me_5)_2M]^+ [PF_6]^-$

| $[(C_5Me_5)_2M]^+ [PF_6]^-$ |      |      |      |      |                                     |                                     |       |
|-----------------------------|------|------|------|------|-------------------------------------|-------------------------------------|-------|
| M                           | Cr   | Mn   | Fe   | Ni   | Ni <sub>0.6</sub> Co <sub>0.4</sub> | Ni <sub>0.9</sub> Co <sub>0.1</sub> | Co    |
| $a$ [Å]                     | 14.7 | 14.5 | 14.3 | 14.5 | 14.2                                | 14.5                                | 14.05 |
| $b$ [Å]                     | 8.9  | 9.0  | 8.9  | 9.0  | 8.8                                 | 8.9                                 | 8.90  |
| $c$ [Å]                     | 8.9  | 9.1  | 9.2  | 9.1  | 9.2                                 | 9.0                                 | 9.12  |

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|             |       |       |       |       |       |       |       |
|-------------|-------|-------|-------|-------|-------|-------|-------|
| $\beta$ [°] | 111.9 | 112.0 | 112.5 | 112.0 | 112.4 | 112.0 | 112.7 |
|-------------|-------|-------|-------|-------|-------|-------|-------|

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