furans and trisubstituted pyrroles that possess an aryl sulfanyl or alkyl sulfanyl substituent at C3 has been developed.

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[9] Typical procedure (**9d**): A mixture of propargyl ketone **9d** (246 mg, 1.0 mmol), CuI (12 mg, 0.05 mmol), and anhydrous DMA (2.0 mL) was stirred in a Wheaton microreactor (3 mL) under an Ar atmosphere at 130 °C. The reaction was monitored by TLC and GC/MS until completion. After 12 h, the mixture was cooled to room temperature and poured into saturated aqueous NH_4Cl (20 mL). The phases were separated, and the aqueous phase was extracted (hexanes, 2×10 mL). The combined organic extracts were washed (brine, 10 mL), dried (Na_2SO_4, 2 g), and concentrated under reduced pressure. The residue was purified by means of silica-gel chromatography with hexanes to give furan **8d** (187 mg, 76 %).

[10] Cycloisomerization of **9j–o** to form pyrroles **8j–o** proceeded under slightly different reaction conditions to those in the synthesis of furans **8a–i**. See Supporting Information for details.

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[14] It was found that EB protecting group can very easily be removed from the pyrroles. Thus, thio-substituted pyrrole **8m** underwent a facile retro-Michael reaction in the presence of KO*t*Bu to give the corresponding pyrrole **8p** quantitatively.

Heterometallic Wheel Complexes

Synthesis and Characterization of Heterometallic $\{Cr_7M\}$ Wheels[**]

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Many beautiful cyclic metal structures have been reported recently, for example, the giant wheels from Müller and co-workers,[1] the wheels using carboxylate ligands made by, among others, the Lippard group,[2] and the metallocoronands reported by Saalfrank and co-workers.[3] One question that intrigued us based on this chemistry was whether heterometallic rings could be made? A recent theoretical paper by Meier and Loss[4] suggests that such wheels may show interesting quantum coherence phenomena. We have found that an extensive family of such wheels can be made straightforwardly, and in good yield, based on the fundamental chemical principle that a cation–anion pair will have different crystallization properties than a neutral molecule.

The neutral homometallic wheel, $[Cr_8F_8(O_2CCMe_3)_{16}]$ (**1**)[5] has been widely studied, both because of its magnetic properties[6] and because it can act as a host for small organic molecules.[7] As we understand the chemistry of **1** thoroughly, it seemed a good candidate for preparing heterometallic analogues. The approach adopted was straightforward; if we replace a single chromium(III) center by a dication (M) the monoanionic species $[Cr_7MF_8(O_2CCMe_3)_{16}]^-$ will be formed. In the presence of a suitable cation, we should then be able to separate the salt from **1**, which may also be present. Using this

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methodology, we have pursued a series of reactions in which metal dications are added to the reaction matrix from which **1** is crystallized.

Two routes have been explored. The first route involves the reaction of hydrated chromium(III) fluoride and $[Ni_2(O_2CCMe_3)_4(HO_2CCMe_3)_4(H_2O)]$ (**2**)[8] or $[Co_2(O_2CCMe_3)_4(HO_2CCMe_3)_4(H_2O)]$ (**3**)[8] in a mixture of DMF and pivalic (trimethylacetic) acid. The reaction gives $[\{Me_2NH_2\}\{Cr_7NiF_8(O_2CCMe_3)_{16}\}]$ (**4**) or $[\{Me_2NH_2\}\{Cr_7CoF_8(O_2CCMe_3)_{16}\}]$ (**5**), respectively, with a trace of **1** that can be removed chromatographically; crystals of **4** or **5** can then be obtained from the eluted solutions. The formation of the $[Me_2NH_2]^+$ ion is presumably as a result of the acid hydrolysis of DMF.

A second, and superior, route is to carry out the reaction of $CrF_3{\cdot}4\,H_2O$ and **2** or **3** in a mixture of a secondary amine and pivalic acid. The reaction was performed in a teflon flask at 140 °C, and the products $[\{R_2NH_2\}\{Cr_7NiF_8(O_2CCMe_3)_{16}\}]$ (where R = Me (**4**), Et (**6**), *n*Pr (**7**), *n*Bu (**8**), *n*-octyl (**9**)) and $[\{R_2NH_2\}\{Cr_7CoF_8(O_2CCMe_3)_{16}\}]$ (where R = Me (**5**), Et (**10**)) crystallize with no trace of **1** or any other impurity. Other secondary amines give similar products.

The chemistry can be extended to other M^{II} ions by dissolving chromium fluoride in the pivalic acid/diethylamine mixture at 140 °C before adding an excess of the second metal salt. $[\{Et_2NH_2\}\{Cr_7MF_8(O_2CCMe_3)_{16}\}]$ (M = Mn (**11**), Fe (**12**), Cd (**13**)) can then be made with good purity in yields of around 70%. For **11** and **12** the hydrated metal chloride salt was used, while for **13** cadmium carbonate was added. We have also made $[\{nBu_2NH_2\}\{Cr_7FeF_8(O_2CCMe_3)_{16}\}]$ (**14**) by this route.

The compounds crystallize in one of four crystal systems: primitive tetragonal, body-centered tetragonal, monoclinic, or orthorhombic.[9] Modeling some of these crystal structures is difficult, mainly because of the nature of the pivalate ligands. The methyl groups are invariably disordered and also create intermolecular voids between the large complexes, presumably containing cocrystallized volatile solvent molecules with no possibility of significant hydrogen bonding. Thus, the solvent atomic positions are ill-defined and impossible to model. Similar problems were encountered for **1**.[7] In the tetragonal crystals the fourfold symmetry of the wheel is higher than that available to the ammonium cation, thus requiring positional disorder in the side arms of the cation. The result is that while refinement proceeded well for **5**, **6**, and **7** (**10**–**13** are isostructural with **6**), for the other structures the *R* factors are high. However, the connectivity among nonhydrogen atoms in the annular structure is unequivocally established in all cases. A view of **6** is shown in Figure 1.

The structure of the anions is similar to that of the neutral wheel **1**, with each M···M vector bridged by a μ-fluoride and two 1,3-bridging pivalates. The M site is disordered over all possible metal sites. In all the structures the average Cr–F and Cr–O bond lengths are longer than in **1**, but not by statistically significant amounts, for example, the average Cr–F bond lengths range from 1.927(5) Å for **8** to 1.939(8) Å for **4** (compared with a range of 1.914(6) and 1.924(5) Å for different solvates of **1**[7]).

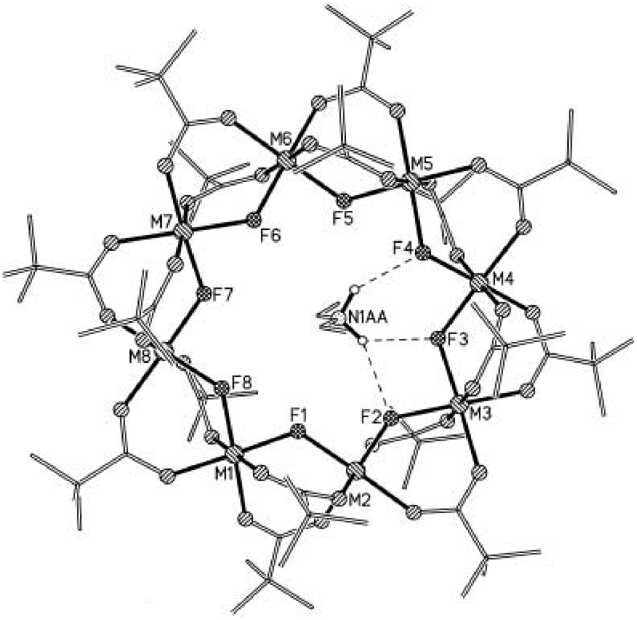

Figure 1. The molecular structure of **6**, with the hydrogen atoms omitted for clarity. Bond length ranges [Å]: $M{-}O(OCH_3)$ 1.940–2.023, $M{-}O(O_2CCH_3)$ 2.021–2.071, (average esd 0.0042). M is 7/8 Cr and 1/8 the second metal at each site.

For all the structures a secondary ammonium cation is found in the cavity of the macrocycle, forming three N–H···F bonds (Figure 1). The N···F distances vary from 2.47 to 3.12 Å, and appear to lengthen as the alkyl side-chains lengthen. The disorder in the structures makes the variation in distances statistically insignificant, however it is clear that in **9** there is barely space to contain the *n*-octyl chains of the cation. The presence of these cations is strong evidence that one of the Cr^{III} centers has been displaced by a dication in each case.

Support for these findings comes from elemental analysis; for all compounds we have analysis of both metals present, C, H, and N, and also F for **4** and **9**–**14**. In all cases, this fits for $[\{R_2NH_2\}\{Cr_7MF_8(O_2CCMe_3)_{16}\}]$. The excellent fluorine analysis rules out the presence of hydroxide in the bridges. Further evidence is provided by mass spectroscopy. For **4**–**14** (**7** not studied) we see the most intense peak for the anion $[Cr_7MF_8(O_2CCMe_3)_{16}]^-$ in the negative-ion spectra, with a correct isotopic distribution. In the positive-ion spectra we see the molecular ion and sometimes peaks at higher mass, indicating the incorporation of Na^+ cations.

Mössbauer spectroscopy of **14** indicates that only Fe^{II} species are present. Both the isotope shift and quadrupole splitting of 1.362 and 2.404 mm s^{-1}, respectively, are clear indications that this oxidation state is present, and there is no evidence of resonance from Fe^{III} ions.

The magnetic behavior of each wheel is broadly similar. For **1**, antiferromagnetic exchange leads to a diamagnetic ground state in zero-field.[6] In the $\{Cr_7Ni\}$ cages the imbalance in spins gives an $S = 1/2$ ground state, leading to an inflection in $\chi_m T$ versus T at low temperature for those cages studied (**4**, **6**, and **7**; Figure 2, data for **6** shown). The behavior can be modeled with one exchange interaction of around 12 cm^{-1},

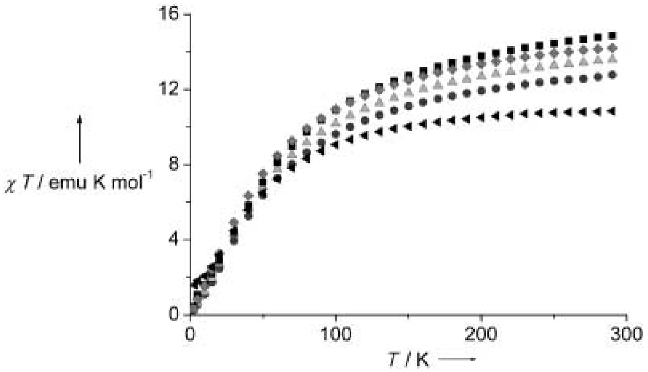

Figure 2. Plot of χ_mT versus T for **6** (●), **10** (▲), **13** (◀), **11** (■), and **14** (◆).

very similar to that reported for **1**.[6] There is no need to invoke a less symmetric magnetic model.

For **10** the high-temperature value of χ_mT is higher than for the $\{Cr_7Ni\}$ wheels, which reflects the presence of high-spin Co^{II} species, but a similar fall is seen at lower temperatures. The ground state of **10** appears to be diamagnetic. For **11** and **14** the value of χ_mT at room temperature is higher still, as high-spin Mn^{II} or Fe^{II} species are present; the low-temperature value again suggests $S = 1$ or 1/2, respectively. For **13** the value of χ_mT at room temperature is lower, as Cd^{II} ions have no spin, while at low temperature the value is equivalent to an $S = 3/2$ ground state.

Complex **1** gives well-defined EPR spectra at low temperatures[6] because of transitions within $S = 1$ and $S = 2$ excited states; the resonances have a relatively low intensity. The EPR spectra of the $\{Cr_7M\}$ wheels are entirely different. For example, **6** gives a pair of transitions at $g_{xy} = 1.781$ and $g_z = 1.740$ (Figure 3a). Therefore the spectrum resembles a transition for an $S = 1/2$ species with axial symmetry. The low g value can be justified based on the vector coupling approach,[10] assuming $g_{Cr} = 1.99$ and $g_{Ni} = 2.10$. A sample of **10** gives a much less intense but identical spectrum resulting from a small percentage (0.04%) of a Ni^{II} impurity. Complexes **11**–**13** give complex spectra consistent with ground states with S greater than 1/2 (Figure 3b, c, and d). For **12** the EPR spectrum contains a broad transition at approximately $g = 4.0$, which indicates the presence of an Fe^{III} impurity (Figure 3b), in addition to features close to $g = 2.00$. The impurity is not found by Mössbauer spectroscopy, however, this may simply reflect the greater sensitivity of EPR analysis. We have not yet fully interpreted the spectra for **11**–**13**.

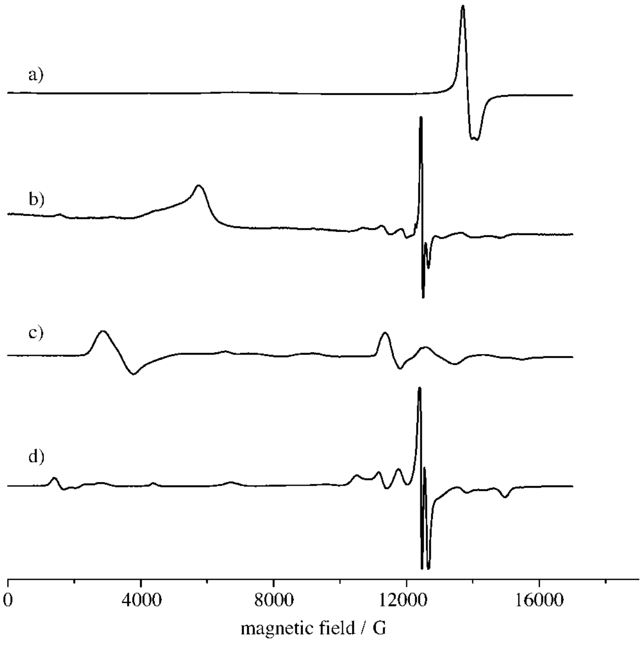

Figure 3. Q-band EPR spectra at 5 K for a) **6**, b) **12**, c) **11**, and d) **13**.

The compounds reported are the first heterometallic wheels. The method used is applicable to many other systems, if a convenient cation can be added to the system. The existence of many such wheels will allow a detailed analysis of the magnetic behavior of antiferromagnetically coupled wheels with a nondiamagnetic ground state. Previously, this has not been possible.

Experimental Section

First route: **4**: $CrF_3{\cdot}4H_2O$ (5.0 g, 27.6 mmol), $[Ni_2(O_2CCMe_3)_4(HO_2CCMe_3)_4(H_2O)]$ (2.0 g, 2.7 mmol), DMF (8.5 mL, 110.0 mmol), and pivalic acid (11.5 g, 112.6 mmol) were heated to 140°C for 2 h while stirring in a teflon flask. During this time, chromium fluoride dissolved and a green crystalline product formed. The solution was cooled to room temperature and the following day the crystalline product was filtered, washed with DMF, then with water, and dried in air. The product was purified by column chromatography on silica gel using toluene as eluent. First the less polar impurity **1** eluted, then **4** (or **5**). The toluene was then evaporated under reduced pressure. Yield 4.0 g (45.3%). The product was recrystallized from from THF/CH_3CN.

Elemental analysis calcd (%) for $C_{82}H_{152}Cr_7F_8NNiO_{32}$: Cr 16.26, Ni 2.62, C 43.99, H 6.84, N 0.63; found: Cr 15.68, Ni 2.32, C 43.74, H 6.96, N 0.55. ES-MS (THF, m/z): −2191 $[Cr_7NiF_8(O_2CCMe_3)_{16}]^-$; +2238 $[M^+]$; +2260 $[M{+}Na]^+$.

5: This product was obtained by an analogous procedure to **4**, but starting from $[Co_2(O_2CCMe_3)_4(HO_2CCMe_3)_4(H_2O)]$. The product was recrystallized from acetone. Yield 3.1 g (35.1%). Elemental analysis calcd (%) for $C_{82}H_{152}CoCr_7F_8NO_{32}$: Cr 16.26, Co 2.62, C 43.99, H 6.84, N 0.63; found: Cr 16.18, Co 2.16, C 44.79, H 7.18, N 0.54. ES-MS (THF, m/z): −2191 $[Cr_7CoF_8(O_2CCMe_3)_{16}]^-$; +2238 $[M^+]$; +2261 $[M{+}Na]^+$.

Second route: **4·C$_6$H$_5$Me**: $CrF_3{\cdot}4H_2O$ (5.0 g, 27.6 mmol), $[Ni_2(O_2CCMe_3)_4(HO_2CCMe_3)_4(H_2O)]$ (2.0 g, 2.7 mmol), dimethylamine (2.0 M solution in THF, 5.5 mL, 11.0 mmol), and pivalic acid (14.0 g, 137.1 mmol) were stirred at 140°C for 5 h. During this time, chromium fluoride dissolved and a green crystalline product formed. The flask was cooled to room temperature and acetone (50 mL) was added while stirring. The crystalline product was filtered, washed with a large quantity of acetone, dried in air, and recrystallized from toluene to give **4**·$C_6H_5CH_3$. Yield 6.45 g (70.1%). Elemental analysis calcd (%) for $C_{89}H_{160}Cr_7F_8N_1Ni_1O_{32}$: Cr 15.62, Ni 2.52, C 45.86, H 6.92, N 0.60, F 6.52; found: Cr 15.17, Ni 2.47, C 46.38, H 7.07, N 0.50, F 6.57. ES-MS (THF, m/z): −2191 $[Cr_7NiF_8(O_2CCMe_3)_{16}]^-$; +2239 $[M^+]$.

5·C$_6$H$_5$Me was obtained by an analogous procedure starting from $[Co_2(O_2CCMe_3)_4(HO_2CCMe_3)_4(H_2O)]$. Yield 6.15 g (66.9%). Elemental analysis calcd (%) for $C_{89}H_{160}Cr_7F_8NCoO_{32}$: Cr 15.61, Co 2.53, C 45.86, H 6.92, N 0.60; found: Cr 15.22, Co 2.45, C 46.66, H 7.24, N 0.58. ES-MS (THF): same as **5**.

Compounds **6–11** were obtained by analogous reactions to that for **4·C_6H_5Me** replacing dimethylamine with the secondary amines listed below.

6: Et_2NH (0.85 g, 11.6 mmol); recrystallized from ethyl acetate. Yield 6.1 g (68.2 %). Elemental analysis calcd (%) for $C_{84}H_{156}Cr_7F_8N_1Ni_1O_{32}$: Cr 15.61, Ni 2.53, C 45.51, H 6.94, N 0.62, F 6.70; found: Cr 14.59, Ni 2.50, C 44.46, H 7.12, N 0.62, F 6.74. ES-MS (THF, m/z): −2191 $[Cr_7NiF_8(O_2CCMe_3)_{16}]^-$; +2266 $[M^+]$; +2289 $[M+Na]^+$.

7: $n$$Pr_2NH$ (1.12 g, 11.1 mmol); recrystallized from toluene. Yield 5.7 g (63.0 %). Elemental analysis calcd (%) for $C_{86}H_{160}Cr_7F_8N_1Ni_1O_{32}$: Cr 15.86, Ni 2.56, C 45.01, H 7.03, N 0.61; found: Cr 15.08, Ni 2.39, C 45.71, H 7.31, N 0.57.

8: $n$$Bu_2NH$ (1.43 g, 11.1 mmol); recrystallized from toluene. Yield 5.65 g (61.7 %). Elemental analysis calcd (%) for $C_{88}H_{164}Cr_7F_8N_1Ni_1O_{32}$: Cr 15.67, Ni 2.53, C 45.50, H 7.12, N 0.60; found: Cr 15.52, Ni 2.46, C 46.92, H 7.31, N 0.59. ES-MS (THF, m/z): −2192 $[Cr_7NiF_8(O_2CCMe_3)_{16}]^-$; +2345 $[M+Na]^+$.

9: (n-octyl)$_2$NH (2.65 g, 11.0 mmol); recrystallized from toluene. Yield 5.45 g (56.7 %). Elemental analysis calcd (%) for $C_{96}H_{180}Cr_7F_8N_1Ni_1O_{32}$: Cr 14.95, Ni 2.41, C 47.35, H 7.45, N 0.58, F 6.24; found: Cr 15.27, Ni 2.34, C 47.93, H 7.52, N 0.56, F 6.36. ES-MS (THF, m/z): −2191 $[Cr_7NiF_8(O_2CCMe_3)_{16}]^-$; +2225 (not assigned).

10 was obtained by an analogous procedure to **5**, replacing Me_2NH with Et_2NH (0.85 g, 11.6 mmol); recrystallized from ethyl acetate. Yield 5.8 g (64.9 %). Elemental analysis calcd (%) for $C_{84}H_{156}Co_1Cr_7F_8N_1O_{32}$: Cr 16.06, Co 2.60, C 44.50, H 6.94, N 0.62, F 6.70; found: Cr 15.31, Co 2.57, C 44.51, H 7.05, N 0.62, F 6.67, Ni 0.04 (impurity). ES-MS (THF, m/z): −2193 $[Cr_7CoF_8(O_2CCMe_3)_{16}]^-$; +2267 $[M^+]$.

11: $CrF_3 \cdot 4H_2O$ (5.0 g, 27.6 mmol), Et_2NH (0.85 g, 11.6 mmol), and pivalic acid (14.0 g, 137.1 mmol) were heated to 140 °C while stirring for 1.5 h in a teflon flask. $MnCl_2 \cdot 4H_2O$ (1.5 g, 7.6 mmol) was added to the mixture and the temperature was increased to 160 °C for 5 h, at which point a green crystalline product had formed. The flask was cooled to room temperature and acetone (50 mL) was added while stirring. The product was collected by filtration, washed with a large quantity of acetone, then dried in air and recrystallized from ethyl acetate. Yield 6.7 g (75.1 %). Elemental analysis calcd (%) for $C_{84}H_{156}Cr_7MnF_8N_1O_{32}$: Cr 16.08, Mn 2.43, C 44.58, H 6.95, N 0.62, F 6.72; found: Cr 16.18, Mn 2.56, C 44.56, H 6.90, N 0.62, F 6.75. ES-MS (THF, m/z): −2188 $[Cr_7MnF_8(O_2CCMe_3)_{16}]^-$; +2262 $[M^+]$; +2284 $[M+Na]^+$.

12 was obtained by an analogous procedure to **11** by replacing $MnCl_2 \cdot 4H_2O$ with $FeCl_2 \cdot 4H_2O$ (1.5 g, 7.5 mmol); recrystallized from ethyl acetate**.** Yield 6.7 g (75.0 %). Elemental analysis calcd (%) for $C_{84}H_{156}Cr_7F_8Fe_1N_1O_{32}$: Cr 16.08, Fe 2.47, C 44.56, H 6.95, N 0.62, F 6.71; found: Cr 15.76, Fe 2.62, C 44.62, H 6.95, N 0.60, F 6.62. ES-MS (THF, m/z): −2188 $[Cr_7FeF_8(O_2CCMe_3)_{16}]^-$; +2263 $[M^+]$; +2287 $[M+Na]^+$.

13 was obtained by an analogous procedure to **11** by replacing $MnCl_2 \cdot 4H_2O$ with $CdCO_3$ (1.2 g, 7.0 mmol); recrystallized from ethyl acetate**.** Yield 6.5 g (67.2 %). Elemental analysis calcd (%) for $C_{84}H_{156}Cr_7CdF_8N_1O_{32}$: Cr 15.69, Cd 4.84, C 43.48, H 6.78, N 0.60, F 6.55; found: Cr 15.22, Cd 4.99, C 43.76, H 6.94, N 0.63, F 6.41. ES-MS (THF, m/z): −2246 $[Cr_7CdF_8(O_2CCMe_3)_{16}]^-$; −2319 $[M^-]$; +2320 $[M^+]$; +2343 $[M+Na]^+$; +2393 (not assigned).

14 was obtained by an analogous procedure to **12** by replacing Et_2NH by $n$$Bu_2NH$ (1.43 g, 11.1 mmol); the product was purified by column chromatography (silica gel/toluene; **14** elutes as the second fraction) then crystallized by evaporation of the toluene. Yield 6.04 g (69.9 %). Elemental analysis calcd (%) for $C_{88}H_{164}Cr_7F_8FeNO_{32}$: Cr 15.69, Fe 2.41, C 45.56, H 7.12, N 0.60, F 6.55; found: Cr 15.35, Fe 2.37, C 46.88, H 7.10, N 0.52, F 6.51. ES-MS (THF, m/z): −2188 $[Cr_7FeF_8(O_2CCMe_3)_{16}]^-$; +2320 $[M^+]$; +2343 $[M+Na]^+$.

Measurements: Mössbauer spectra were measured at 80 K against a ^{57}Co(Rh) source moving at constant acceleration. Velocity calibration was carried out by using the resonance lines of metallic iron, and isomer shifts are given relative to iron metal at room temperature. EPR spectra were recorded at 5 K on a Bruker ESP 300E spectrometer at the X-, K-, and Q-bands (approximately 9.5, 24, and 34 GHz, respectively) and at the W-band (approximately 90 GHz) using a homemade spectrometer.[11]

Magnetic susceptibility measurements were performed on polycrystalline samples in the temperature range 2.0–298 K in an applied field of 1 T using a Quantum Design MPMS SQUID magnetometer. Corrections for diamagnetic contributions were applied by using Pascal's Constants. The sample holder diamagnetism was measured and subtracted from the raw data.

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[9] Crystal data for **4** ($C_{82}H_{152}Cr_7F_8NNiO_{32}$; $M_r = 2232.05$): dark green plate, tetragonal, space group $P4$, $a = b = 19.8908(5)$, $c = 16.0395(8)$ Å, $V = 6345.9(4)$ Å^3, $Z = 2$ (the molecule lies on a fourfold axis), $T = 120.0(2)$ K, $\rho_{calcd} = 1.168$ g cm^{-1}, $F(000) = 2342$, $\mu(Mo_{K\alpha}) = 0.730$ mm^{-1}. Crystal data for **5** ($C_{82}H_{152}CoCr_7F_8NO_{32}$; $M_r = 2232.05$): dark-green plate, tetragonal, space group $I4$, $a = b = 19.8514(7)$, $c = 16.1783(7)$ Å, $V = 6375.5(4)$ Å^3, $Z = 2$ (the molecule lies on a fourfold axis), $T = 120.0(2)$ K, $\rho_{calcd} = 1.163$ g cm^{-1}, F(000) = 2342, $\mu(Mo_{K\alpha}) = 0.726$ mm^{-1}. Crystal data for **6** ($C_{87}H_{158}Cr_7F_8NNiO_{33}$; $M_r = 2314.14$): dark green plate, monoclinic, space group $P2_1/c$, $a = 24.9959(10)$, $b = 16.6134(7)$, $c = 30.8822(13)$ Å, $\beta = 109.957(1)$°, $V = 12054.2(9)$ Å^3, $Z = 4$, $T = 120.0(2)$ K, $\rho_{calcd} = 1.275$ g cm^{-1}, $F(000) = 4860$, $\mu(Mo_{K\alpha}) = 0.771$ mm^{-1}. Crystal data for **7** ($C_{92}H_{166}Cr_7F_8NNiO_{33}$; $M_r = 2382.26$): dark green plate, monoclinic, space group $P2_1/c$, $a = 25.2406(18)$, $b = 16.7224(11)$, $c = 31.593(2)$ Å, $\beta = 101.661(1)$°, $V = 13059.8(15)$ Å^3, $Z = 4$, $T = 120.0(2)$ K, $\rho_{calcd} = 1.212$ g cm^{-1},

$F(000) = 5012$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.714\ \mathrm{mm^{-1}}$. Crystal data for **8** ($C_{88}H_{164}Cr_7F_8NNiO_{32}$; $M_r = 2316.20$): dark-green plate, monoclinic, space group $P2_1/n$, $a = 26.067(2)$, $b = 20.3010(17)$, $c = 27.098(2)$ Å, $\beta = 112.258(1)°$, $V = 13271.5(19)$ Å^3, $Z = 4$, $T = 120.0(2)$ K, $\rho_{\mathrm{calcd}} = 1.159\ \mathrm{g\,cm^{-1}}$, $F(000) = 4876$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.700\ \mathrm{mm^{-1}}$. Crystal data for **9** ($C_{96}H_{180}Cr_7F_8NNiO_{32}$; $M_r = 2428.41$): dark-green plate, orthorhombic, space group *Pnma*, $a = 23.2504(15)$, $b = 21.0031(13)$, $c = 31.451(2)$ Å, $V = 15358.4(17)$ Å^3, $Z = 4$, $T = 120.0(2)$ K, $\rho_{\mathrm{calcd}} = 1.050\ \mathrm{g\,cm^{-1}}$, $F(000) = 5132$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.608\ \mathrm{mm^{-1}}$. Unit cell for **10**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.031(1)$, $b = 16.639(1)$, $c = 30.910(1)$ Å, $\beta = 110.03(1)°$. Unit cell for **11**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.061(4)$, $b = 16.622(3)$, $c = 30.960(5)$ Å, $\beta = 110.488(5)°$. Unit cell for **12**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.049(2)$, $b = 16.630(1)$, $c = 30.927(2)$ Å, $\beta = 110.18(3)°$. Unit cell for **13**: dark-green plate, monoclinic, space group $P2_1/c$, $a = 25.173(7)$, $b = 16.629(5)$, $c = 31.135(8)$ Å, $\beta = 111.093(3)°$. Compounds **10**, **11**, **12**, and **13** are isostructural with **6**. Data were collected on a Bruker SMART CCD diffractometer ($\mathrm{Mo_{K\alpha}}$, $\lambda = 0.71069$ Å). In all cases the selected crystals were mounted onto the tip of a glass pin using Paratone-N oil and placed in the cold flow (120 K) produced with an Oxford Cryocooling device. Complete hemispheres of data were collected using ω scans (0.3°, 30 s/frame). Integrated intensities were obtained with SAINT+[12] and corrected for absorption using SADABS.[12] Structure solution and refinement was performed with the SHELX-package.[12] The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 to give for **4**: using 479 parameters and 55 restraints, $wR_2 = 0.5006$ (12935 unique reflections), $R_1 = 0.1806$ (11281 reflections with $I > 2\sigma(I)$); for **5**: using 299 parameters and 28 restraints, $wR_2 = 0.2937$ (7978 unique reflections), $R_1 = 0.0973$ (7306 reflections with $I > 2\sigma(I)$); for **6**: using 1204 parameters and 105 restraints, $wR_2 = 0.1716$ (20413 unique reflections), $R_1 = 0.0804$ (17353 reflections with $I > 2\sigma(I)$); for **7**: using 901 parameters and 108 restraints, $wR_2 = 0.3241$ (22002 unique reflections), $R_1 = 0.1140$ (13892 reflections with $I > 2\sigma(I)$); for **8**: using 827 parameters and 116 restraints, $wR_2 = 0.4806$ (30385 unique reflections), $R_1 = 0.1661$ (17629 reflections with $I > 2\sigma(I)$); for **9**: using 449 parameters and 76 restraints, $wR_2 = 0.5085$ (9688 unique reflections), $R_1 = 0.1780$ (7500 reflections with $I > 2\sigma(I)$). CCDC-191618–191623 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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14-Electron Platinum(II) Complexes

Novel T-Shaped 14-Electron Platinum(II) Complexes Stabilized by One Agostic Interaction**

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Three-coordinate 14-electron d^8-ML_3 complexes, which are generally transient species generated in situ by ligand dissociation, have received much attention because of their key role in many stoichiometric and catalytic reactions.[1] Platinum(II) complexes of the form $[L_2PtR(\text{solvent})]^+$, which contain bidentate nitrogen ligands and a weakly bonded solvent molecule, have been found to be active in alkane C–H activation through the formation of the transient alkane σ-adduct $[L_2PtR(R'{-}H)]^+$.[2] Such species have eluded isolation because of the ease of displacement of the alkane moiety by solvent or anions in solution, and thus, several approaches have been used to examine their reactivity including the study of agostic complexes.[3] Orpen and Spencer have described a series of β-agostic platinum(II) complexes of the type $[Pt(R)(P{-}P)]^+$ (P–P = chelating diphosphane; R = alkyl), which are in equilibrium with the corresponding alkene–hydrido derivatives,[4] and which have been viewed as models for intermediates along the migratory insertion/β-elimination alkene-polymerization pathway.[3a,4c] The bulky phosphane P*t*Bu$_3$ has been used to stabilize 14-electron T-shaped platinum(II) species of the form *trans*-$[PtH(P\textit{t}Bu_3)_2]X$ (X = noncoordinating anion), which have been characterized by NMR analysis.[5] It is noteworthy that the analogous derivatives bearing PCy_3 or P*i*Pr$_3$ moieties led to the four-coordinate complexes *trans*-$[PtH(PR_3)_2(\text{solvent})][BAr^f_4]$ (R = Cy,[6a] *i*Pr;[6b] $Ar^f = 3{,}5\text{-}(CF_3)_2C_6H_3$), with dichloromethane as solvent.

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