Synthesis and Magnetic Properties of 1 : 1 Salts containing the Bis(η^6-hexamethylbenzene)cobalt Cation†

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The salts $[Co(\eta^6-C_6Me_6)_2]^+[A]^-$ (A = BPh_4, NbF_6, PF_6 or SbF_6) have been prepared from anhydrous $CoCl_2$. Solid-state magnetic susceptibility measurements on these salts indicate that they all obey the Curie–Weiss law in the temperature range 30–300 K with μ_{eff} = 2.7, 2.8, 2.8 and 2.6 μ_B with corresponding θ values of −1.4, 0.2, −4.1 and 0.4 K for the BPh_4^-, NbF_6^-, PF_6^- and SbF_6^- salts respectively. Below 20 K, the magnetic susceptibility for all the salts deviate substantially from the Curie–Weiss law. The experimental susceptibility data for the compounds $[Co(\eta^6-C_6Me_6)_2]^+[BPh_4]^-$ and $[Co(\eta^6-C_6Me_6)_2]^+[NbF_6]^-$ can be fitted to a model in which the $^3A_{2g}$ triplet ground state assigned to the $[Co(\eta^6-C_6Me_6)_2]^+$ moiety exhibits a positive zero-field splitting of 17.8 and 20.5 cm^{-1} respectively. In contrast, the magnetic susceptibilities for $[Co(\eta^6-C_6Me_6)_2]^+[A]^-$ (A = PF_6 or SbF_6) cannot be fitted to this model in the range 2–30 K due to more significant intermolecular antiferromagnetic spin–spin interactions. All the salts were EPR silent at between 4 and 300 K both in the solid state and in frozen solution. Reaction of $[Co(\eta^6-C_6Me_6)_2]^+[PF_6]^-$ with either $[NBu_4][tcnq]$ (tcnq = tetracyano-*p*-quinodimethane) or $[NBu_4][C_3\{C(CN)_2\}_3]$ [$C_3\{C(CN)_2\}_3$ = tris(dicyanomethylene)cyclopropane] gave insoluble paramagnetic precipitates with μ_{eff} = 4.1 and 4.5 μ_B and θ values of −12.9 and −3.5 K respectively.

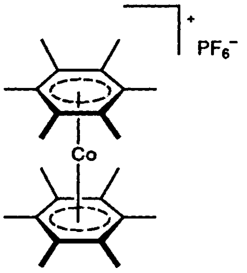
The electronic ground states of the paramagnetic metallocenes $[M(\eta^5-C_5H_5)_2]$ (M = V, Cr, Mn, Co or Ni) have been extensively investigated by use of solid-state magnetic susceptibility and EPR studies.[1] A rich variety of electronic structure and behaviour has been observed. For example, manganocene $[Mn(\eta^5-C_5H_5)_2]$ exhibits both high-spin $^6A_{1g}$ or low-spin $^2E_{2g}$ ground states depending on the cyclopentadienyl ring substituents.[2] Magnetic susceptibility studies on chromocene and cobaltocene show deviations from the Curie law at low temperatures which have been attributed to a dynamic Jahn–Teller distortion.[3] Pure chromocene and cobaltocene are EPR silent in the solid state but exhibit complex anisotropic host-dependent absorbances when magnetically diluted in diamagnetic host lattices.[4] The 20-electron nickelocene has been proposed to exhibit large zero-field splitting of its $^3A_{2g}$ triplet ground state on the basis of variable-temperature magnetic susceptibility measurements.[5]

These early magnetic studies have proved all the more significant in the light of subsequent observations that the organometallic charge-transfer salts containing the decamethylmetallocenium cations $[M(\eta-C_5Me_5)_2]^+$ (M = Fe, Mn or Cr) and planar organic radical anions such as those of tetracyanoethylene (tcne), tetracyano-*p*-quinodimethane (tcnq) and hexacyanobuta-1,3-diene $[C_4(CN)_6]$ have been shown to possess remarkable magnetic and electronic properties.[6] For example, the tcne salts of $[M(\eta-C_5Me_5)_2]^+$ (M = Cr, Fe or Mn) exhibit three-dimensional ferromagnetic ground states with Curie temperatures (T_C) of 3.6, 4.8 and 8.8 K respectively.[7] The increase in T_C for the salts $[M(\eta-C_5Me_5)_2][tcne]$ (M = Fe or Mn) has been attributed to the increase in spin multiplicity of the metallocenium cation. Simple mean field theory predicts that T_C should be proportional to the exchange integral J and the spin [as $S(S + 1)$]. Consequently, we are interested in the synthesis and characterisation of novel organometallic charge-transfer salts containing high-spin multiplicity cations.

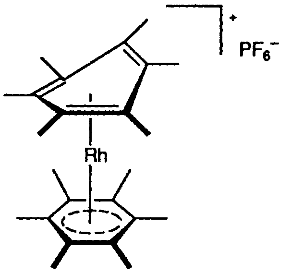
In contrast to the charge-transfer salts based on metallocenium cations, to date no molecular charge-transfer salts containing bis(η-arene)metal cations have been shown to exhibit cooperative three-dimensional magnetic ordering.[8] In this paper we report our efforts on the synthesis and magnetic properties of salts containing the triplet (S = 1) bis(η-arene)metal cation $[Co(\eta^6-C_6Me_6)_2]^+$.

Results and Discussion

The formally 20-electron $[Co(\eta^6-C_6Me_6)_2]^+$ cation was initially reported by Fischer and Lindner[9] in 1964 and later in 1970 by Anderson and Drago.[10] The structure remained unknown until 1980 when Muetterties and co-workers[11] reported the single-crystal X-ray structure determination of $[Co(\eta^6-C_6Me_6)_2]^+[PF_6]^-$ in which he observed both hexamethylbenzene ligands to be symmetrically bonded to the metal centre in an η^6 fashion. This contrasts with the crystal structure determination of $[Rh(C_6Me_6)_2]^+[PF_6]^-$ which was shown[11] to be $[Rh(\eta^6-C_6Me_6)(\eta^4-C_6Me_6)]^+[PF_6]^-$ giving a diamagnetic 18-electron configuration.



$[Co(\eta^6-C_6Me_6)_2]^+[PF_6]^-$



$[Rh(\eta^6-C_6Me_6)(\eta^4-C_6Me_6)]^+[PF_6]^-$

A qualitative molecular-orbital scheme for the $[Co(\eta^6-C_6Me_6)_2]^+$ cation (Fig. 1) assuming D_{6h} symmetry suggests that it is formally a 20-electron compound and would be predicted to adopt a $^3A_{2g}$ electronic ground state. In the context of preparing novel molecular charge-transfer complexes that exhibit cooperative ferromagnetic interactions the stabilisation of triplet states in the solid state is believed to be one of the

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† *Non-SI unit employed:* $\chi_{SI} = \chi_{cgs} \times 4\pi \times 10^{-6}$; $\mu_B \approx 9.27402 \times 10^{-24}$ J T^{-1}

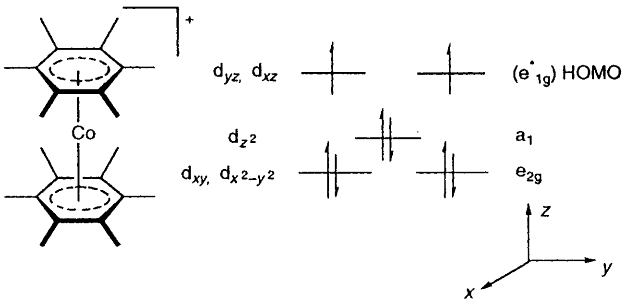

Fig. 1 Qualitative frontier-molecular-orbital diagram for $[Co(\eta^6\text{-}C_6Me_6)_2]^+$

Table 1 Summary of magnetic susceptibility data for compounds **1**–**6**

Compound	$\mu_{eff}{}^a/\mu_B$	θ^a/K	$\langle g\rangle^b$	D^b/cm^{-1}
1	2.7	−1.4	1.87	17.8
2	2.8	0.2	1.98	20.5
3	2.8	−4.1		
4	2.6	0.4		
5	4.1	−12.9		
6	4.5	−3.5		

[a] Derived from least-squares fitting to the Curie–Weiss law between 30 and 300 K. [b] Obtained from least-squares fitting to equation (1).

important prerequisites. Consequently, we were interested in preparing and studying the magnetic properties of salts containing the $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ cation.

Synthesis and Characterisation of the 1 : 1 *Salts* $[Co(\eta^6\text{-}C_6Me_6)_2]^+[A]^-$ ($A = BPh_4, NbF_6, PF_6$ *or* SbF_6).—*Synthesis.* Treatment of anhydrous $CoCl_2$ with Al, C_6Me_6 and $AlCl_3$ generates the $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ cation.[9] Salts containing this cation can be isolated by addition of $NaBPh_4$, NH_4NbF_6, NH_4PF_6 or $NaSbF_6$ giving bright yellow microcrystals of $[Co(\eta^6\text{-}C_6Me_6)_2]^+[A]^-$ ($A = BPh_4, NbF_6, PF_6$ or SbF_6) **1**–**4**. Compounds **2**–**4** are air-stable solids but rapidly decompose in all solvents except CH_2Cl_2. However, compound **1** is stable in air for short periods only and decomposes in all solvents except CH_2Cl_2.

Magnetic susceptibility measurements. The magnetic susceptibility of solid samples of compounds **1**–**4** have been measured in the temperature range 2.0–300 K using a SQUID magnetometer at fields in the range 0.1–1.0 T (Table 1). The magnetic susceptibility data for compounds **1** and **2** can be fitted to the Curie–Weiss expression, $\chi_M = C/(T - \theta)$, in the temperature range 30–300 K with $\mu_{eff} = 2.7$ and 2.8 μ_B and $\theta = -1.4$ and 0.2 K respectively (Fig. 2). The magnetic moments are close to the spin-only value of 2.83 μ_B which is consistent with the qualitative molecular-orbital picture (Fig. 1) which predicts a $^3A_{2g}$ electronic ground state for compounds **1**–**4**. However, below 30 K the magnetic susceptibility data for compounds **1** and **2** deviate substantially from the Curie–Weiss law. Fig. 3 shows the low-temperature molar magnetic susceptibility data for compound **1**.

We initially investigated the possibility that the cations in **1** and **2** were undergoing a structural distortion such as an η^6–η^4 shift of the hexamethylbenzene ligand. Such a distortion would remove the degeneracy of the A_{2g} highest occupied molecular orbital (HOMO) and cause spin-pairing resulting in a magnetically inactive singlet ($S = 0$) ground state. The temperature dependence of the magnetic susceptibility for systems undergoing thermally activated triplet–singlet crossover can be described by the Bleaney–Bowers expression. In fact, we were not able to fit the data to the Bleaney–Bowers relationship and conclude that $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ is stable with respect to η^6–η^4 ring shifts.

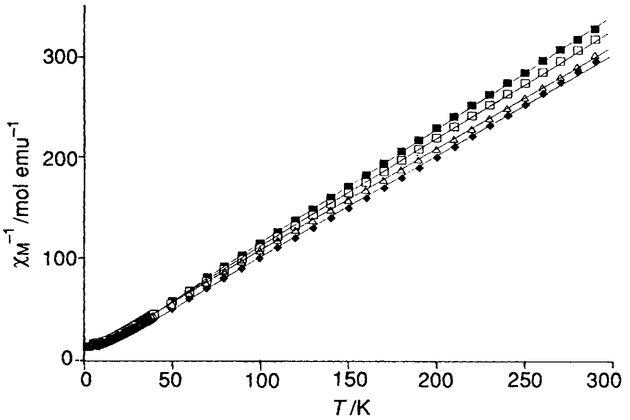

Fig. 2 Plot of χ_M^{-1} *versus* T (5–300 K) for compounds **1** (■), **2** (◆), **3** (□) and **4** (△); the straight lines are the least-squares fits to the Curie–Weiss law

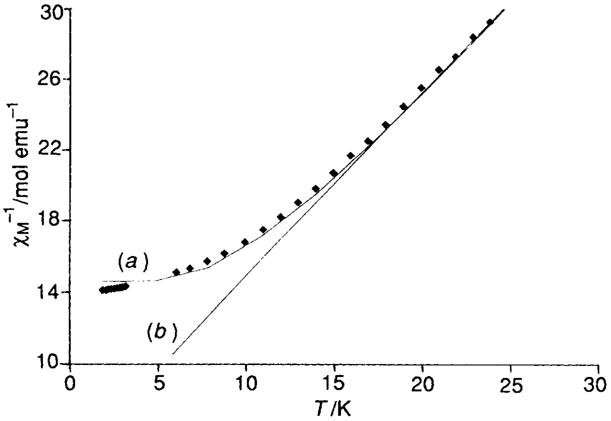

Fig. 3 Plot of χ_M^{-1} *versus* T (2–25 K) for compound **1** (◆); (*a*) equation (1) and (*b*) the least-squares fit to the Curie–Weiss law (20–300 K)

We believe that the magnetic susceptibility behaviour is analogous to that reported for $[Ni(\eta\text{-}C_5H_5)_2]$ at low temperatures.[5] Using the nickelocene analogy we have constructed an energy-level diagram for the $^3A_2$ ground state under the influence of both internal and external fields (Fig. 4). Neglecting the differences between $g_{\parallel}$ and $g_{\perp}$ an expression can be derived for the temperature dependence of the molar magnetic susceptibility $\langle\chi_M\rangle$ from a randomly orientated microcrystalline sample as a function of a parameter (D) which is a measure of the zero-field splitting of the ground state [equation (1)].[12]

$$\langle\chi\rangle = \left(\frac{2Ng^2\mu_B{}^2}{3kT}\right)\left[\frac{\frac{2}{x} - \frac{2\exp(-x)}{x} - \exp(-x)}{1 + 2\exp(-x)}\right] \qquad (1)$$

Plots of χ^{-1} *versus* T are linear at high temperature and deviate when $D/kT\,(=x)\rightarrow 1$. Least-squares fitting of the experimental susceptibility data to equation (1) gave values of 17.8 and 20.5 cm^{-1} for the zero-field splitting (D) and 1.87 and 1.98 for the isotropic g tensor ($\langle g\rangle$) for complexes **1** and **2** respectively. A similar analysis of the magnetic susceptibility data for nickelocene gave a value of $D = 25$ cm^{-1}.[5]

The magnetic susceptibility data for compounds **3** and **4** also obey the Curie–Weiss expression in the temperature range 20–300 K, with $\mu_{eff} = 2.8$ and 2.6 μ_B and $\theta = -4.1$ and 0.4 respectively. At temperatures between 2 and 20 K the data cannot be fitted to equation (1) for compounds **3** and **4** respectively. Below 5 K the experimental data deviate substantially from the values predicted by this expression (Fig. 5 shows the molar susceptibility for compound **4**). In this

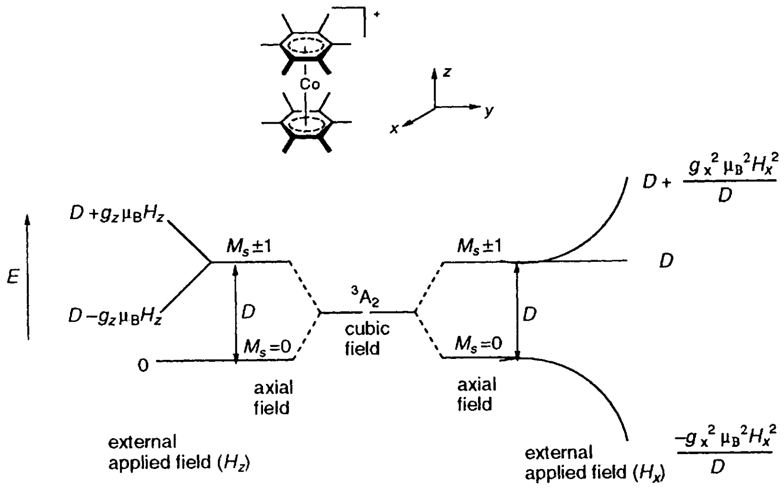

Fig. 4 Splitting diagram for the HOMO ($^3A_{2g}$) in $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ with internal axial field and external magnetic field

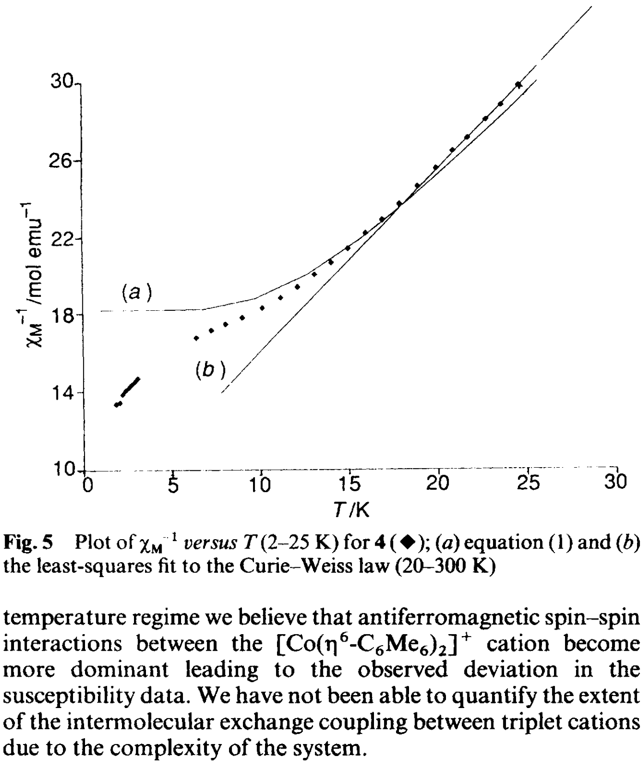

Fig. 5 Plot of χ_M^{-1} *versus* T (2–25 K) for **4** (◆); (*a*) equation (1) and (*b*) the least-squares fit to the Curie–Weiss law (20–300 K)

temperature regime we believe that antiferromagnetic spin–spin interactions between the $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ cation become more dominant leading to the observed deviation in the susceptibility data. We have not been able to quantify the extent of the intermolecular exchange coupling between triplet cations due to the complexity of the system.

EPR Spectroscopy. Compounds **1**–**4** do not exhibit EPR signals in either frozen solution or the solid state in the temperature range 4–300 K. This observation is in agreement with the prediction that triplet-spin systems exhibiting a large positive zero-field splitting (> 7 cm^{-1}) do not show EPR absorptions.

Reaction of $[Co(\eta^6\text{-}C_6Me_6)_2]^+[PF_6]^-$ **3** *with* $[NBu_4][tcnq]$ *and* $[NBu_4][C_3\{C(CN)_2\}_3]$.—A solution of compound **3** in CH_2Cl_2 was added to an equimolar solution of $[NBu_4][tcnq]$ in CH_2Cl_2. An immediate black precipitate **5** formed which was found to be insoluble in all common organic solvents. The infrared spectrum of **5** contains resonances assignable to ν(C≡N) stretches at 2197 and 2120 cm^{-1}, however the frequencies were not in agreement with any of the known salts of tcnq. In addition, the elemental microanalysis data could not be fitted to any discrete molecular composition.

Reaction of compound **3** with equimolar amounts of $[NBu_4][C_3\{C(CN)_2\}_3]$ in CH_2Cl_2 also yields a blue-purple precipitate **6** which was found to be insoluble in all common organic solvents. The infrared spectrum showed the blue-purple solid contained resonances assignable to ν(C≡N) stretches at 2214 and 2185 cm^{-1}, however the frequencies were not in agreement with any of the known salts of the $[C_3\{C(CN)_2\}_3]^-$ anion. In addition, the elemental microanalysis data could not be fitted to any discrete molecular composition.

Magnetic susceptibility measurements. In view of the recent report that the amorphous solid of approximate formulation $[V(tcne)_2]\cdot 1\text{-}2CH_2Cl_2$ formed by the reaction of tcne with $[V(C_6H_6)_2]$ exhibits room-temperature ferromagnetism,[13] we decided to measure the magnetic susceptibility of compounds **5** and **6**. The magnetic susceptibilities were measured in the temperature range 6–320 K. The molar susceptibility (assuming a 1 : 1 salt) can be fitted to the Curie–Weiss law, $\chi_M = C/(T-\theta)$, with $\mu_{eff} = 4.1$ and $4.5\ \mu_B$, $\theta = -12.9$ and -3.5 K for **5** and **6** respectively. The effective moments are significantly larger than the 3.31 μ_B predicted for a 1 : 1 charge-transfer salt containing non-interacting $S = 1$ cations and $S = \frac{1}{2}$ anions. The magnetisation *versus* field data at low temperature show no evidence for cooperative magnetic interaction in **5** or **6**.

Conclusion

Compounds **1**–**4** have been shown to exhibit triplet ($^3A_{2g}$) ground states in the temperature range 5–300 K. Surprisingly we observed no evidence for an η^6–η^4 ring shift to give an 18-electron configuration as observed for $[Rh(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]^+[PF_6]^-$. At low temperature, compounds **1** and **2** show evidence for significant zero-field splitting of the $^3A_{2g}$ ground state, while compounds **3** and **4** show evidence for more dominant intermolecular antiferromagnetic exchange interactions between the $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ cations below 5 K.

Experimental

General.—The reactions were carried out in an inert atmosphere of nitrogen by the use of a vacuum line or inert atmosphere dry-box. Solvents were pre-dried over molecular sieves (type 4 Å) and refluxed with drying agents under a continuous stream of nitrogen. Dichloromethane was dried by refluxing over P_2O_5, and acetonitrile by refluxing over CaH_2. Solvents were distilled prior to use and were stored over molecular sieves in flame-dried ampoules under nitrogen.

Equipment.—Magnetic susceptibility measurements were performed on a Cryogenic Consultants SQUID (superconducting quantum interference device) magnetometer. Typically *ca.* 12–15 mg of sample were placed in Suprasil™ quartz buckets under nitrogen. The susceptibilities were corrected for the intrinsic diamagnetism of the sample holder. Temperature-independent corrections such as the diamagnetism of the electronic cores of the constituent atoms (χ_{diam}) and temperature-independent paramagnetism (χ_{tip}) were estimated by extrapolation of the high-temperature susceptibility ($T \longrightarrow \infty$). EPR spectra were obtained using an X-band Varian spectrometer fitted with an Oxford Instruments cryostat. The samples were prepared under nitrogen and run in 4 mm Suprasil™ quartz tubes fitted with a Young's Teflon stopcock. Infrared spectra were recorded on a Mattson Instruments Polaris spectrometer as mulls in Nujol between NaCl plates. Elemental microanalyses were performed by the Analytical Services of the Inorganic Chemistry Laboratory.

Syntheses.—$[Co(\eta^6\text{-}C_6Me_6)_2]^+[BPh_4]^-$ **1**. Anhydrous $CoCl_2$ (1.3 g, 10 mmol), C_6Me_6 (10 g, 62 mmol), $AlCl_3$ (9.3 g, 70 mmol) and Al powder (0.45 g, 17 mmol) were mixed together in a 100 cm^3 Schlenk flask and stirred at 160 °C for 4 h. The dark brown mixture was then allowed to cool and solidify. This brown solid was pulverised in a mortar under N_2. The resulting powder was added slowly to methanol (120 cm^3) at 60 °C. The yellow-green solution formed was allowed to warm slowly to 0 °C over 4 h. Water (180 cm^3) was added to precipitate the excess C_6Me_6. The mixture was then filtered and added to a concentrated aqueous solution of $NaBPh_4$ (6.8 g in 40 cm^3 H_2O) giving a bright yellow precipitate. The precipitate was collected by filtration, washed with water (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3) and dried *in vacuo*. The crude salt can be recrystallised from CH_2Cl_2–diethyl ether at −40 °C giving $[Co(\eta^6\text{-}C_6Me_6)_2]^+[BPh_4]^-$ **1** (0.75 g, 1.1 mmol, 11%) [Found (calc.) for $C_{48}H_{56}BCo$: C, 81.3 (82.0); H, 8.2 (8.0)%].

$[Co(\eta^6\text{-}C_6Me_6)_2]^+[NbF_6]^-$ **2**. Anhydrous $CoCl_2$ (0.65 g, 5 mmol), C_6Me_6 (5 g, 31 mmol), $AlCl_3$ (4.66 g, 35 mmol) and Al powder (0.225 g, 8.5 mmol) were mixed together in a 100 cm^3 Schlenk flask and stirred at 160 °C for 4 h. The dark brown mixture was then allowed to cool and solidify. This brown solid was pulverised in a mortar under N_2. The resulting powder was added slowly to methanol (60 cm^3) at −60 °C. The yellow-green solution formed was allowed to warm slowly to 0 °C over 4 h. Water (90 cm^3) was added to precipitate the excess C_6Me_6. The mixture was then filtered and added to a concentrated solution of NH_4NbF_6 (2.25 g in 20 cm^3 H_2O, 10 mmol) giving a bright yellow precipitate. The precipitate was isolated quickly, since if the solution is left long enough (45 min) it turns green and there is decomposition. Hence very low yields were obtained. The yellow precipitate was collected by filtration, washed with water (2 × 10 cm^3), diethyl ether (2 × 10 cm^3) and dried *in vacuo* to yield $[Co(\eta^6\text{-}C_6Me_6)_2]^+[NbF_6]^-$ **2** (0.185 g, 0.3 mmol, 6%) [Found (calc.) for $C_{24}H_{36}CoF_6Nb$: C, 48.7 (48.8); H, 6.2 (6.1)%].

$[Co(\eta^6\text{-}C_6Me_6)_2]^+[PF_6]^-$ **3**. The procedure of Fischer and Lindner[9] was followed with certain modifications. Anhydrous $CoCl_2$ (1.3 g, 10 mmol), C_6Me_6 (10 g, 62 mmol), $AlCl_3$ (9.3 g, 70 mmol) and Al powder (0.45 g, 17 mmol) were mixed together in a 100 cm^3 Schlenk flask and stirred at 160 °C for 4 h. The dark brown mixture was then allowed to cool and solidify. This brown solid was pulverised in a mortar under N_2. The resulting powder was added slowly to methanol (120 cm^3) at −60 °C. The yellow-green solution formed was allowed to warm slowly to 0 °C over 4 h. Water (180 cm^3) was added to precipitate the excess C_6Me_6. The mixture was then filtered and added to a concentrated aqueous solution of NH_4PF_6 (3.4 g, in 20 cm^3 H_2O) giving a bright yellow precipitate. The precipitate was collected by filtration, washed with water (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3) and dried *in vacuo*. The crude salt can be recrystallised from CH_2Cl_2–diethyl ether at −40 °C giving $[Co(\eta^6\text{-}C_6Me_6)_2]^+[PF_6]^-$ **3** (1 g, 2 mmol, 20%) [Found (calc.) for $C_{24}H_{36}CoF_6P$: C, 54.4 (54.5); H, 7.05 (6.9)%].

$[Co(\eta^6\text{-}C_6Me_6)_2]^+[SbF_6]^-$ **4**. Anhydrous $CoCl_2$ (0.65 g, 5 mmol), C_6Me_6 (5 g, 31 mmol), $AlCl_3$ (4.66 g, 35 mmol) and Al powder (0.225 g, 8.5 mmol) were mixed together in a 100 cm^3 Schlenk flask and stirred at 160 °C for 4 h. The dark brown mixture was then allowed to cool and solidify. This brown solid was pulverised in a mortar under N_2. The resulting powder was added slowly to methanol (60 cm^3) at −60 °C. The yellow-green solution formed was allowed to warm slowly to 0 °C over 4 h. Water (90 cm^3) was added to precipitate the excess C_6Me_6. The mixture was then filtered and added to a concentrated solution of $NaSbF_6$ (2.59 g in 20 cm^3 H_2O, 10 mmol) giving a pale yellow precipitate. The precipitate was collected by filtration, washed with water (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3) and dried *in vacuo*. The crude salt can be recrystallised from CH_2Cl_2–diethyl ether at −40 °C giving $[Co(\eta^6\text{-}C_6Me_6)_2]^+[SbF_6]^-$ **4** (0.3 g, 0.5 mmol, 10%) [Found (calc.) for $C_{24}H_{36}CoSb$: C, 45.9 (46.5); H, 6.1 (5.9)%].

Attempted preparation of $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ $[tcnq]^-$. Compound **3** (0.2 g, 0.4 mmol) and $[NBu_4][tcnq]$ (0.169 g, 0.4 mmol) were dissolved in CH_2Cl_2 and mixed together at room temperature. An immediate black powder precipitated. The powder was filtered off, washed thoroughly with diethyl ether (3 × 10 cm^3) and dried *in vacuo*. The precipitate **5** was found to be insoluble in all common solvents. The elemental analysis figures (Found: C, 60.2; H, 4.2; Co, 12.7; N, 14.7%) did not correspond to any trial formulations.

Attempted preparation of $[Co(\eta^6\text{-}C_6Me_6)_2]^+$-$[C_3\{C(CN)_2\}_3]^-$. Compound **3** (0.2 g, 0.4 mmol) and $[NBu_4][C_3\{C(CN)_2\}_3]$ (0.178 g, 0.4 mmol) were dissolved in CH_2Cl_2 and mixed together at room temperature then cooled to −40 °C for 7 d. A blue-purple powder **6** formed which was collected by filtration and washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo* (yield 0.050 g) [Found (calc.): C, 63.9 (70.7); H, 5.7 (5.9); Co, 10.0 (9.6); N, 13.9 (13.8)%].

Acknowledgements

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