Synthesis and Characterisation of Cyclopentadienylcobalt and Pentamethylcyclopentadienylcobalt Diselenolenes

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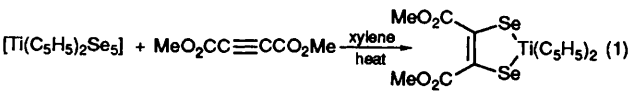
Reaction of $[\mathrm{Co(C_5R^1_5)(CO)_2}]$ (R^1 = H or Me) with 1,2,3-selenadiazoles in toluene under reflux in the presence of an excess of elemental selenium leads in moderate yield to the diselenolenes $[\mathrm{Co(C_5R^1_5)\{SeC(R^2){=}C(R^3)Se\}}]$ [R^2–R^3 = $(\mathrm{CH_2})_6$, $\mathrm{CH{=}CH(CH_2)_4}$ or $\mathrm{CH{=}CH(CH_2)_2CH{=}CH}$; R^2 = Ph, R^3 = H; $R^2 = R^3$ = Ph]. In particular this procedure provides access to novel compounds without electron-withdrawing substituents. The products have been characterised by ^{1}H NMR, IR, UV/VIS and mass spectroscopy, microanalysis and cyclic voltammetry. Each diselenolene undergoes a fully reversible one-electron reduction, and exhibits a low-energy electronic transition at *ca.* 800 nm. Of the substituents (R^1,R^2,R^3), R^1 has the greatest influence on the spectroscopic and electrochemical properties. For structurally similar compounds there is a linear correlation between the half-wave potential for the reduction and the energy of the first electronic absorption band.

Considerable attention has been devoted to transition-metal dithiolenes over the past twenty-five years.[1] This interest has been prompted by their potentially useful electrochemical and optical properties. Transition-metal bis(dithiolenes) have been used both for preparing molecular superconductors,[2] and in passive Q-switch and mode-locking applications.[3] By contrast, studies of the selenium analogues of dithiolenes (diselenolenes) have been relatively rare.

The most readily accessible compounds of this type are the benzene-1,2-diselenolate derivatives, and they have been investigated by a number of research groups.[4] The synthesis of selenium analogues of 4,5-dimercapto-1,3-dithiole-2-thionate is also comparatively straightforward.[5] Davison and Shawl[6] prepared a number of compounds containing the 1,2-bis(trifluoromethyl)ethene-1,2-diselenolate ligand, but this required the use of boiling selenium (b.p. 685 °C!) at an intermediate stage. An alternative route to this ligand has since been reported,[7] and the behaviour of several of its complexes has been investigated.[8] More recently, the synthesis of transition-metal diselenolenes has been achieved *via* the addition of selenium to activated alkynes[9,10] [equations (1) and (2)]. A cyclopentadienylcobalt diselenolene has also been prepared[11] from an intermediate biscarbyne cluster[12] [equation (3)] by a related process.



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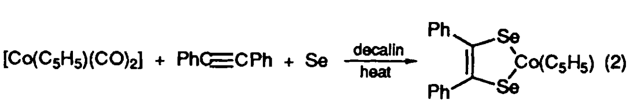

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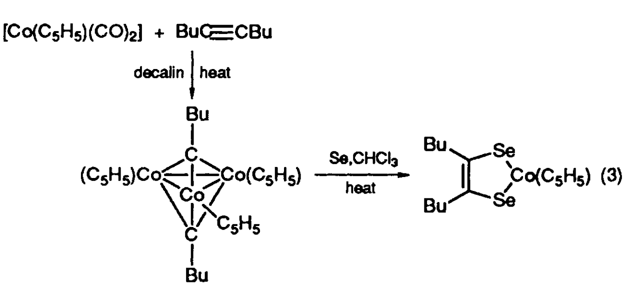

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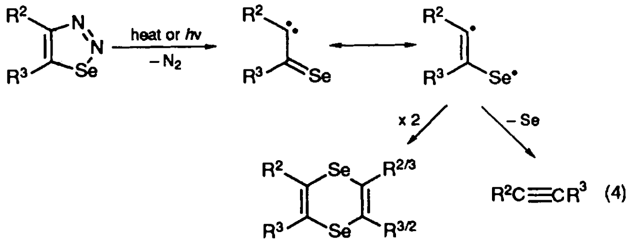
We are engaged in a study of the interaction of 1,2,3-selenadiazoles with organotransition-metal complexes.[13] 1,2,3-Selenadiazoles generally react *via* elimination of dinitrogen and it is the fate of the selenaketocarbene intermediate thus produced which determines the outcome of the reaction. In the absence of other reagents, alkynes or 1,4-diselenins are the usual products[14] [equation (4)]. We have examined the use of



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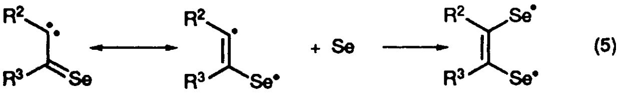
1,2,3-selenadiazoles as a potential source of diselenolate ligands, on the basis of the formal relationship shown in equation (5), and we now present the results of our investigations. A preliminary account of this work has been published.[15]



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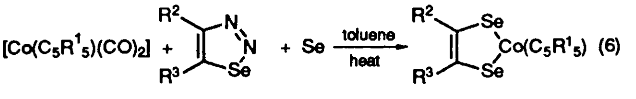
Results and Discussion

Treatment in refluxing toluene of $[\mathrm{Co(C_5R^1_5)(CO)_2}]$ (R^1 = H or Me) with one of a range of 1,2,3-selenadiazoles, in the presence of an excess of elemental selenium, leads to the formation of the diselenolenes **1–9** [equation (6), Fig. 1]. At



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1–9

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Table 1 Analytical and mass spectroscopic data

Complex	Colour	Yield (%)	M.p./°C	Analysis[a] (%) C	Analysis[a] (%) H	Mass spectra[b]
1	Royal blue	25	128	40.10 (40.00)	4.40 (4.40)	392 (M^+, 56), 284 [$Co(C_5H_5)Se_2^+$, 100], 124 [$Co(C_5H_5)^+$, 76]
2	Royal blue	32	168	38.65 (40.25)	3.85 (3.90)	390 (M^+, 48), 284 [$Co(C_5H_5)Se_2^+$, 100], 124 [$Co(C_5H_5)^+$, 95]
3	Royal Blue	34	170	40.10 (40.45)	3.45 (3.40)	388 (M^+, 26), 284 [$Co(C_5H_5)Se_2^+$, 42], 185 ($C_8H_9Se^+$, 100), 124 [$Co(C_5H_5)^+$, 84]
4	Dark green	28	126	44.75 (46.95)	5.85 (5.90)	462 (M^+, 35), 354 ($C_{10}H_{15}CoSe_2^+$, 100), 133 ($C_{10}H_{13}^+$, 85)
5	Dark green	44	158	47.25 (47.20)	5.55 (5.50)	460 (M^+, 10), 354 ($C_{10}H_{15}CoSe_2^+$, 12), 43 ($C_3H_7^+$, 100)
6	Dark green	59	214	47.30 (47.40)	5.10 (5.10)	458 (M^+, 27), 354 ($C_{10}H_{15}CoSe_2^+$, 48), 133 ($C_{10}H_{13}^+$, 100)
7[c]	Blue (lit: blue)	7	130 (lit: 116–118)	40.75 (40.65)	2.95 (2.90)	386 (M^+, 5), 284 [$Co(C_5H_5)Se_2^+$, 14], 149 ($C_7H_6Co^+$, 100)
8[c]	Blue (lit: purple, green)	10	242 (lit: 237, 250–255)	48.80 (49.60)	3.55 (3.30)	462 (M^+, 5), 284 [$Co(C_5H_5)Se_2^+$, 20], 178 ($C_{14}H_{10}^+$, 100), 124 [$Co(C_5H_5)^+$, 22]
9	Green	11	214	46.65 (47.60)	4.35 (4.65)	456 (M^+, 3), 354 ($C_{10}H_{15}CoSe_2^+$, 4), 149 ($C_7H_6Co^+$, 100)

[a] Required values in parentheses. [b] Data presented as: *m*/*z* assignment, relative abundance; *m*/*z* values are for isotopomers containing ^{80}Se; expected isotope distribution patterns are observed. [c] See Ref. 10.

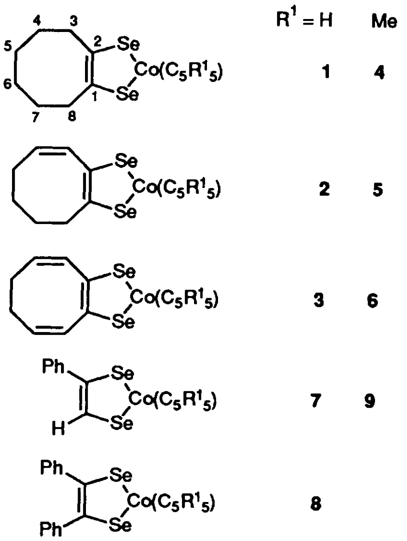
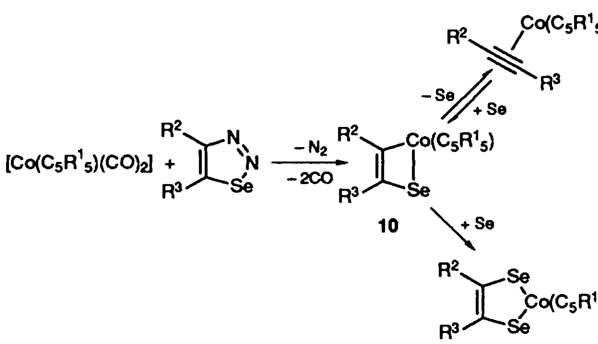


Fig. 1 Structures of diselenolenes **1**–**9**



(7)

least a five-fold excess of selenium is required to minimise the formation of unwanted by-products. The yields are moderate (see Table 1), but in general rather better for the pentamethylcyclopentadienylcobalt derivatives. The $Co(C_5Me_5)$ analogue of **8** could not however be obtained by this route. The cyclopentadienylcobalt derivatives may also be prepared from [$Co(C_5H_5)(PPh_3)_2$].

The mechanism of these reactions is still unclear, but evidence from related studies involving sulfur indicates that the C–Se bond in the putative selenaketocarbene intermediate does not remain intact.[16] The free alkyne is unlikely to be formed, since for example in ethylene glycol cycloocteno-1,2,3-selenadiazole only begins to decompose at temperatures above 150 °C.[17] We therefore presume that both C–Se bond scission and formation occur within the co-ordination sphere of the transition metal. A possible mechanism incorporating these features is shown in equation (7). A platinum complex analogous to the intermediate **10** has been isolated and characterized.[18]

Compounds **7** and **8** have previously been obtained in comparable yield by an alternative route using the corresponding alkyne.[10] The synthesis of **1**–**6**, however, represents a rare preparation of diselenolenes which do not bear electron-withdrawing substituents.[7,11] Pentamethylcyclopentadienylcobalt diselenolenes were apparently unknown before this work although related dithiolenes have been prepared.[19]

Compounds **1**–**9** are crystalline, intensely coloured (blue or green) solids with sharp melting points, soluble in common organic solvents. Dissolution in non-polar media is slow, which may imply some association in the solid state, but we have been unable to obtain X-ray quality crystals in order to verify this. Solutions of **1**–**9** decompose within a few hours of exposure to air, although crystalline samples appear to be indefinitely stable. Microanalytical and mass spectroscopic data are summarised in Table 1, and are in accord with the proposed formulations. The molecular ion is observed in each case; fragmentation *via* loss of the alkyne $R^2C{\equiv}CR^3$ is also common to all the compounds. It is notable that only the cyclopentadienylcobalt derivatives give rise to an observable fragment $Co(C_5R^1{}_5)^+$.

Proton NMR and IR spectroscopy have also been used to characterize the diselenolenes **1**–**9**, and the results are summarised in Tables 2 and 3. Two distinct trends may be discerned. For compounds **1**–**3** the effect of increasing unsaturation in the cyclooctene ring is to shift the cyclopentadienyl proton resonance to slightly lower field. On the other hand, changing the substituents on the cyclopentadienyl ring has a much larger influence on the cyclooctene protons. Protons H^3 and H^8 are shifted upfield by 0.11–0.14 ppm in the $Co(C_5Me_5)$ derivatives **4**–**6**. This effect is amplified on considering the H^1 resonance of **7** and **9**: introduction of the methyl groups produces an upfield shift of 0.69 ppm.

Table 2 Proton NMR spectroscopic data^a (300 MHz, $CDCl_3$)

Complex	Assignment
1	1.18 (4 H, m, H^5,H^6), 1.72 (4 H, m, H^4,H^7), 3.10 (4 H, m, H^3,H^8), 5.24 (5 H, s, C_5H_5)
2	1.33 (2 H, m, H^6), 1.71 (2 H, m, H^7), 1.89 (2 H, m, H^5), 3.12 (2 H, m, H^8), 5.26 (5 H, s, C_5H_5), 5.83 (1 H, m, H^4), 6.63 [1 H, d, *J*(HH) = 11.4 Hz, H^3]
3	2.19 (4 H, m, H^5, H^6), 5.28 (5 H, s, C_5H_5), 5.94 (2 H, m, H^4, H^7), 6.81 [2 H, d, *J*(HH) = 11.4 Hz, H^3, H^8]
4	1.17 (4 H, m, H^5,H^6), 1.65 (4 H, m, H^4,H^7), 1.92 [15 H, s, $C_5(CH_3)_5$]
5	1.34 (2 H, m, H^6), 1.64 (2 H, m, H^7), 1.89 (2 H, m, H^5), 1.91 [15 H, s, $C_5(CH_3)_5$], 2.98 (2 H, m, H^8), 5.69 (1 H, m, H^4), 6.52 [1 H, d, *J*(HH) = 11.6 Hz, H^3]
6	1.90 [15 H, s, $C_5(CH_3)_5$], 2.24 (4 H, m, H^5,H^6), 5.82 (2 H, m, H^4,H^7), 6.70 [2 H, d, *J*(HH) = 11.4 Hz, H^3,H^8]
7^b	5.36 (5 H, s, C_5H_5), 7.28–7.71 (5 H, m, C_6H_5), 9.87 [1 H, s, ^2J(SeH) = *ca.* 40 Hz, H^1]
8^b	5.36 (5 H, s, C_5H_5), 7.18 (10 H, m, C_6H_5)
9	1.95 [15 H, s, $C_5(CH_3)_5$], 7.25–7.69 (5 H, m, C_6H_5), 9.18 [1 H, s, ^2J(SeH) = 40.2 Hz, ^3J(SeH) < 3 Hz, H^1]

^{a} For numbering scheme for assignments, see Fig. 1. ^{b} See Ref. 10.

Table 3 Infrared spectroscopic data^a

Complex	Selected absorption maxima (cm^{-1})^b
1	2921vs, 2839s, 1581s, 1501s, 1438s, 1404s, 1341m, 1257m, 1105m, 998s, 830s, 811vs, 407m
2	2983m, 2914vs, 2842s, 1556m, 1433w, 1416m, 1346w, 1260m, 1098s, 828s, 808vs, 734w
3	2923vs, 2824s, 1552s, 1441w, 1414m, 1354w, 1261w, 1099m, 1049w, 815vs, 709m
4	2960m, 2917vs, 2842s, 1515s, 1454s, 1444m, 1369s, 1351s, 1259m, 1096m, 1020s, 800m, 444m
5	2979m, 2907vs, 2843s, 1508m, 1448m, 1372vs, 1350s, 1254w, 1126w, 1013m, 807w, 726m, 442w
6	2957m, 2915vs, 2848s, 2827m, 1504w, 1462m, 1447m, 1374vs, 1355s, 1260s, 1104m, 1053m, 1017s, 801s, 726m, 715m
7^c	1641m, 1533s, 1479m, 1436m, 1421m, 1408m, 1192m, 1051m, 1010m, 993m, 832s, 814s, 759s, 728s
8^c	1482m, 1431m, 1404m, 1049m, 997w, 832s, 759s, 723s
9	2958m, 2923m, 2853w, 1730w, 1462m, 1377m, 1259s, 1097s, 1018s, 803s, 761m, 748m

^{a} Recorded on KBr discs. ^{b} Abbreviations: w, weak; m, medium; s, strong; vs, very strong. ^{c} See Ref. 10.

Table 4 Ultraviolet–visible spectroscopic data^a

	Absorption maxima (nm)^b			
Complex	Band 1	2	3	4
1	823 (2.602)	601 (3.607)	495 (2.886)	296 (3.898)
2	830 (2.663)	615 (3.531)	495 (2.903)	298 (4.011)
3	841 (2.568)	631 (3.415)	495 (2.799)	300 (3.987)
4	763 (2.574)	634 (3.415)	463 (2.724)	302 (3.851)
5	773 (2.932)	638 (3.724)	463 (3.073)	305 (4.301)
6	782 (2.519)	650 (3.785)	454 (2.833)	308 (4.398)
7^c	819 (2.362)	607 (3.301)	481 (2.699)	298 (3.919)
8^c	809 (2.230)	618 (3.207)	476 (2.732)	295 (3.732)
9	757 (2.653)	632 (3.446)	452 (2.740)	306 (4.079)

^{a} Recorded as pentane solutions (10^{-4}–10^{-3} mol dm^{-3}). ^{b} log (ε/dm^3 mol^{-1} cm^{-1}) given in parentheses. ^{c} See Ref. 10.

In the ^1H NMR spectra of **7** and **9** coupling of H^1 to a ^{77}Se nucleus ($I = \frac{1}{2}$, 7.6% abundant) has been resolved with *J*(SeH) *ca.* 40 Hz. This may be identified as a two-bond coupling to the geminal selenium atom, by comparison with values of ^2J(SeH) in 4-phenyl- and 4-methyl-1,2,3-selenadiazole.[20] Coupling to the vicinal selenium may only be distinguished as a broadening of the observed resonance, implying that the three-bond coupling constant, ^3J(SeH) < 3 Hz. Coupling ^2J(SeH) in both **7**, **9** and the corresponding 1,2,3-selenadiazole is significantly greater than ^2J(SeH) in vinylic selenides (typically *ca.* 20 Hz).[21] The low field shift and large ^2J(SeH) for H^1 are characteristic of a proton attached to an aromatic heterocycle. For the diselenolenes **7** and **9** this is further evidence of electron delocalisation in the diselenametallacycle.

Ultraviolet–visible spectroscopic data for **1**–**9** are summarised in Table 4. The spectra are dominated by an intense band at about 300 nm; three lower energy transitions are responsible for the vivid colours of these compounds. A strong absorption in the near infrared is characteristic of many bis(dithiolenes): this band is generally assigned to an intraligand π–π* transition, and may be shifted to longer wavelengths by the introduction of conjugating substituents.[22] The lowest energy band for **1**–**9** is possibly of similar origin: increasing the unsaturation of the cyclooctene ring produces a bathochromic shift in the spectra of **1**–**6**. On the other hand, phenyl substituents, as in **7**–**9**, have the opposite effect. Further studies will be required to clarify the assignment. It is clear, however, that the greatest effect on the spectra is obtained by permethylating the cyclopentadienyl ring. Average shifts of −59, +25, −33 and +7 nm are observed for bands 1, 2, 3 and 4 respectively. The dithiolene analogue of **1** has previously been prepared;[16] replacement of selenium by sulfur produces shifts of −83, −19, −76 and −2 nm. A common origin for bands 1 and 3, and for bands 2 and 4, appears to be indicated.

Dithiolenes have a rich electrochemistry: many complexes show a fully reversible three- or four-membered redox series. This is of course related to the low energy of the first electronic transition in the absorption spectra and reflects the relatively small highest-occupied–lowest-unoccupied molecular orbital (HOMO–LUMO) gap. Cyclic voltammetry has been used to examine the behaviour of compounds **1**–**9**. In all cases, a single reversible one-electron reduction is observed. The results are summarised in Table 5. Most measurements were carried out in acetonitrile solution, but dimethylformamide (dmf) was found to be a more suitable solvent for the phenyl-substituted derivatives **7**–**9**. When referenced to ferrocene–ferrocenium, there was no dependence of the half-wave potential on the solvent. At a scan rate of 100 mV s^{-1} and a temperature of 25 °C, peak-to-peak separations ($E_{pa} - E_{pc}$) for **1**–**9** were, on average, *ca.* 85 mV in acetonitrile and *ca.* 75 mV in dimethylformamide. Whilst these values are slightly larger than the 59 mV expected for a one-electron process, they were comparable with $E_{pa} - E_{pc}$ for the ferrocene–ferrocenium couple under the same conditions. The ratios of the anodic and cathodic peak currents were close to unity, and lowering the scan rate had no significant effect on the peak-to-peak separations. Convolution/deconvolution of the data confirmed that the reduction of **1**–**9** is fully reversible. In the absence of ferrocene, an ill-defined irreversible oxidation wave was revealed: this correlates with the results of other workers.[23]

Sugimori and co-workers[23] have studied the effects of substituents on the reduction half-wave potentials of cyclopentadienylcobalt dithiolenes and diselenolenes. There is a linear correlation between $E_{\frac{1}{2}}$ values and substituent parameters. This is borne out by the data in Table 5. Electron-withdrawing substituents make $E_{\frac{1}{2}}$ less negative; electron-donating substituents have the opposite effect. As was noted previously with regard to the spectroscopic data, the largest change is brought about by permethylating the ring (average shift = −0.27 V), or by replacing selenium with sulfur: the dithiolene analogue of **1** has $E_{\frac{1}{2}} = -1.37$ V.[16] Cobalt-59 spectroscopy has been used to determine directly the electron density at the metal atom in a related series of compounds.[24] It was concluded that only those atoms or groups bonded directly to cobalt exert a significant influence. Our results are in accord with these findings.

The possibility of a correlation between spectral and redox

Table 5 Cyclic voltammetric data[a]

Complex	Measured half-wave potentials (V)	
	MeCN	dmf
1	−1.24	—
2	−1.18	−1.20
3	−1.15	—
4	−1.52	—
5	−1.46	−1.47
6	−1.40	−1.43
7	*b*	−1.12
8	−1.08[b]	−1.14
9	—	−1.40

[a] With respect to internal ferrocene standard. [b] Lit. values:[23] **7**, −1.11 V; **8**, −1.10 V.

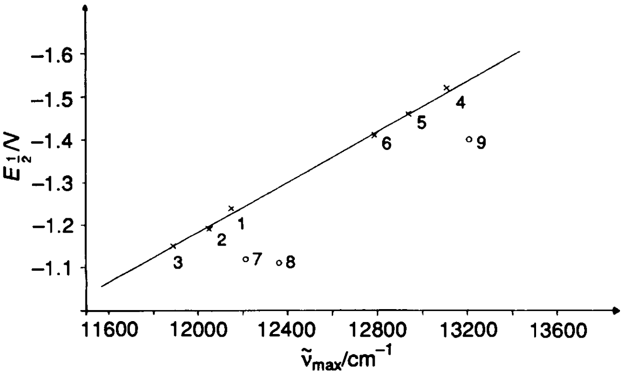


Fig. 2 Plot of reduction half-wave potential *vs.* energy of the first electronic transition for diselenolenes **1–9**

properties of co-ordination compounds has been discussed by Vlcek.[25] A charge-transfer transition is in one sense an intramolecular redox process, and it may be expected that the same factors will be involved in lowering the transition energy as make the intermolecular process more favourable. Values of $E_{\frac{1}{2}}$ are plotted against $\tilde{\nu}_{max}$ (band 1) for compounds **1–9** in Fig. 2. The data for **1–6** lie on a good straight line. These compounds are structurally extremely similar, so that the effects of solvation are constant throughout the series. The phenyl-substituted diselenolenes do not appear to fulfil this criterion, and the data for **7–9** lie outside the linear correlation.

Conclusion

The use of 1,2,3-selenadiazoles provides a useful route to cyclopentadienylcobalt and pentamethylcyclopentadienylcobalt diselenolenes, and in particular provides access to compounds without electron-withdrawing substituents. The spectroscopic and electrochemical properties of the products **1–9** are primarily determined by the immediate environment of the cobalt atom, although variation of the substituents does produce limited, and in part, predictable effects. We are currently investigating the chemical behaviour of **1–9**, and the extent to which the synthetic method used in their preparation is of general applicability.

Experimental

All reactions were performed using standard Schlenk techniques and predried solvents under an atmosphere of dinitrogen. Alumina used for column chromatography was pretreated with 2% H_2O. Proton NMR spectra: Nicolet AM300, tetramethylsilane as internal standard. UV/VIS spectra: Perkin Elmer Lambda 9. IR spectra: Perkin Elmer 983G. Mass spectra: MS902 operating at 70 eV (*ca.* 1.12 × 10^{-17} J). Melting points (uncorrected): Electrothermal apparatus. Microanalyses: Perkin Elmer PE240.

Cyclic voltammetry was performed using apparatus comprising: EG & G Princeton Applied Research model 362 scanning potentiostat; IBM PS2 computer using Condecon 300 software; platinum working and auxiliary electrodes; Ag–AgCl reference electrode; test solution containing 1 × 10^{-3} mol dm^{-3} analyte, 1 × 10^{-3} mol dm^{-3} ferrocene as internal standard, 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. Under these conditions the ferrocene–ferrocenium couple has $E_{\frac{1}{2}}$ = +0.45 V (acetonitrile), and $E_{\frac{1}{2}}$ = +0.48 V (dimethylformamide) relative to Ag–AgCl.

Cycloocteno-1,2,3-selenadiazole,[14] 6,7,8,9-tetrahydrocycloocta-1,2,3-selenadiazole,[26] 6,7-dihydrocycloocta-1,2,3-selenadiazole,[27] 4-phenyl-1,2,3-selenadiazole,[28] 4,5-diphenyl-1,2,3-selenadiazole,[29] dicarbonylcyclopentadienylcobalt[30] and dicarbonyl(pentamethylcyclopentadienyl)cobalt[31] were prepared by literature methods.

Cyclopentadienylcobalt Diselenolenes (**1–3**, **7**, **8**) *and Pentamethylcyclopentadienylcobalt Diselenolenes* (**4–6**, **9**).—In a typical experiment, solutions of dicarbonylcyclopentadienylcobalt (0.27 g, 1.5 mmol) and cycloocteno-1,2,3-selenadiazole (0.33 g, 1.5 mmol) in toluene (total volume 60 cm^3) were mixed. Powdered selenium (0.60 g, 7.5 mmol) was added and the mixture heated under reflux for 4 h. Removal of the solvent under reduced pressure left an intensely coloured oily solid, which was purified by column chromatography. Using a 3:1 mixture of light petroleum (b.p. 40–60 °C) and toluene two bands were eluted. The first, yellow band contained a small amount of the by-product bis(cycloocteno)-1,4-diselenin.[14] The second, blue band yielded cyclooctene-1,2-diselenolato(cyclopentadienyl)cobalt **1** as a royal blue solid, which could be recrystallised from pentane at −30 °C.

Cycloocta-1,3-diene-1,2-diselenolato(cyclopentadienyl)cobalt **2**, cycloocta-1,3,7-triene-1,2-diselenolato(cyclopentadienyl)-cobalt **3**, phenylethene-1,2-diselenolato(cyclopentadienyl)-cobalt **7** and 1,2-diphenylethene-1,2-diselenolato(cyclopentadienyl)cobalt **8** were each prepared by an analogous procedure using the corresponding 1,2,3-selenadiazole. The dark green pentamethylcyclopentadienyl derivatives (**4–6**, **9**) were similarly obtained from dicarbonyl(pentamethylcyclopentadienyl)cobalt. Attempts to prepare 1,2-diphenylethene-1,2-diselenolato(pentamethylcyclopentadienyl)cobalt, the analogue of **8**, were unsuccessful. Yields, spectroscopic and analytical data are summarised in Tables 1–5.

Acknowledgements

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