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# Diastereoisomer separation and absolute configuration of (*ortho*- and (*meta*-$MeC_6H_4CO_2Me)Cr(CO)_2L$ (L = (+)-neomenthyl-$PPh_2$)

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## Abstract

Replacement of a carbonyl ligand by (+)-neomenthyl$PPh_2$ provides a method for diastereoisomer separation of the methyl esters of (*ortho*- and (*para*-toluic acid)$Cr(CO)_3$. The absolute planar configurations have been assigned.

## Introduction

Application of (arene)$Cr(CO)_3$ complexes in organic synthesis continues to be an area of active interest [1a–1c*]. The electron-withdrawing nature of the $Cr(CO)_3$ group increases the susceptibility of the ring towards metalation [2a–2e*] or nucleophile addition [3a–3d*], increases the acidity of benzylic hydrogens [4a–4d*], and additionally provides a high diastereoselectivity both in nucleophilic addition to the complexed ring and in reactions at the benzylic position of conformationally restricted complexes (*ortho*-disubstituted [5a–5c*] or fused ring systems) [4b*,4c*,6]. The use of such complexes in enantioselective synthesis depends also on the availability of resolved complexes of known planar chirality. Such complexes have been prepared in resolved or enriched form by classical resolution using crystalliza-

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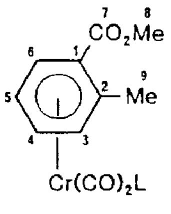
* Reference numbers with an asterisk refer to notes in the list of references.

tion or chromatography of complexes possessing suitable functionality (COX; X = OH, H, R) [7a–7e], by chirality transfer during the *ortho*-substitution of monosubstituted complexes possessing a chiral substituent [2b], by chirality transfer during complexation using chiral *ortho*-disubstituted arenes [4c,8,9*], and most recently by enzymatic resolution [10].

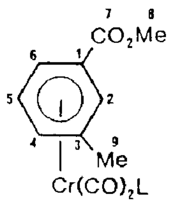
We recently described [11a,11b] a method for diastereoisomer separation of asymmetric (diene)Fe$(CO)_3$ complexes using the monosubstituted derivative formed on replacement of a carbonyl ligand by NMDPP[(+)-neomenthyldiphenylphosphine]. We show here that this method is also applicable to the (arene)Cr$(CO)_3$ series, as illustrated for the methyl esters of (*ortho*- and (*meta*-toluic acid)Cr$(CO)_3$.

## Results and discussion

The NMDPP complexes **1c**, **1d** and **2c**, **2d** and the model $PPh_3$ complexes **1b** and **2b**, can be prepared in good yield by photolysis of the tricarbonyl in the presence of a slight excess of phosphine [12a–12d*]. The equimolar diastereoisomer pairs can be separated by preparative TLC; except for **1d**, their extreme solubility in hydrocarbon solvents prevents crystallization. Indeed, a single crystallization of **1c**, **1d** from petroleum ether (60–80 °C) yields material which is 85% enriched in **1d**. The strong molecular ions in the mass spectra of these complexes can also be used for analytical characterization. Though distinct resonances may be observed for each diastereoisomer in the $^{31}$P, $^{13}$C and $^{1}$H NMR spectra (Table 1), diastereoisomeric purity is mostly easily assessed from the $^{1}$H NMR spectra using the $CO_2Me$ resonance for **1c**, **1d** and the ring methyl resonance for **2c**, **2d**. Relative to the tricarbonyl, all complexes exhibit the previously observed [12d*] upfield shift of ring carbon and proton resonances which is consistent with the poorer electron-withdrawing character of the $Cr(CO)_2PR_3$ moiety. For all the phosphine-substituted complexes, two CO resonances are observed. The carbonyl ligands are not exchanged by rapid arene ring rotation [13a,13b*], which does, however, equilibrate energetically accessible eclipsed and staggered conformations of the ring relative to the $Cr(CO)_2L$ moiety.



(1a) L=CO
(b) L=PPh₃
(c) L=NMDPP (1R)
(d) L=NMDPP (1S)



(2a) L=CO
(b) L=PPh₃
(c) L=NMDPP (1R)
(d) L=NMDPP (1S)

(1S configurations shown)

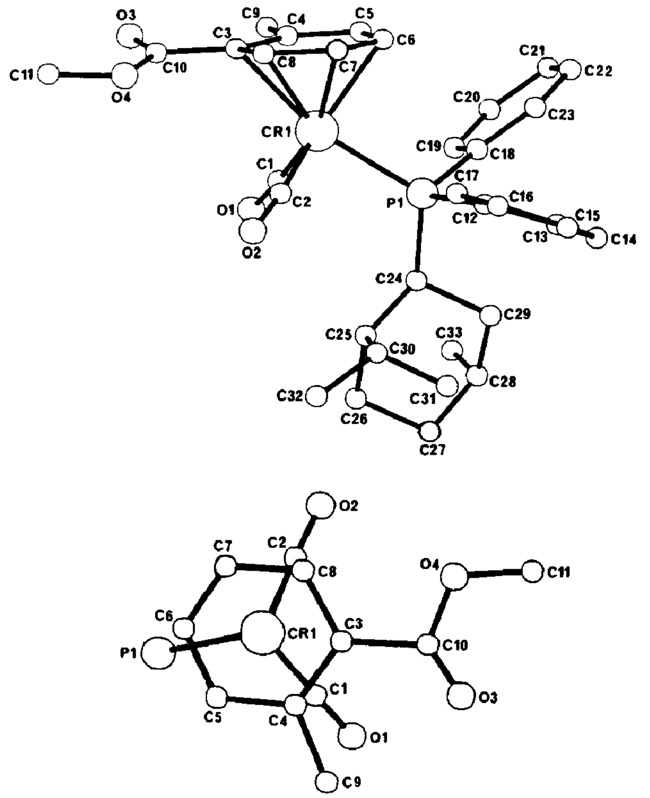
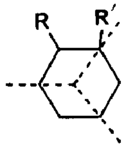


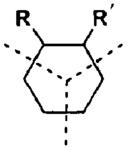
Fig. 1. Molecular structure of complex **1d**.

The absolute configurations of **1c**, **1d** have been determined by a crystal structure analysis of **1d** (Fig. 1). The data are sufficiently precise (see Experimental) to provide the absolute configuration of both the neomenthyl group (1*S*,2*S*,5*R*) and the planar chirality (1*S*), though the configuration of the neomenthyl group is, of course, known.

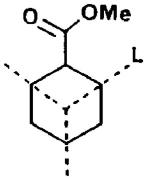
The approximate eclipsing of the ring methyl by a carbonyl of the $Cr(CO)_2L$ moiety is consistent with structural data on other *ortho*-disubstituted complexes which, in the absence of steric effects [14a–14d*], show conformation **3** in which CO eclipses the more strongly electron-donating substituent [15a–15c], or, the staggered conformation **4**, in cases where electronic and steric effects are approximately equal [16a–16e].



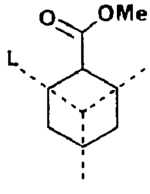
(3)



(4)



(5) anti



(6) syn

Structural studies on several (methylbenzoate)$Cr(CO)_2L$ complexes also show (with one exception) [17] an eclipsed conformation **5**, with L either *syn* (L = CS,

Table 1

Spectroscopic data

| Complex | Infrared (cm$^{-1}$) | $^{13}$C NMR (ppm) [c] | | $^{1}$H NMR (ppm) [d] | | $^{31}$P NMR (ppm) [e] |
|---|---|---|---|---|---|---|
| **1a** | 1978 [a] | 1 | 111.9 | 3,4 | 4.02–4.20(m) | – |
| | 1900 | 2 | 90.1 | 5 | 4.59(td) | |
| | | 3–6 | 96.6 | 6 | 5.69(dd) | |
| | | | 95.5 | $CO_2Me$ | 3.33(s) | |
| | | | 92.3 | Me | 2.60(s) | |
| | | | 87.6 | | | |
| | | 7 | 166.3 | | | |
| | | 8 | 52.5 | | | |
| | | 9 | 21.2 | | | |
| | | CO | 231.2 | | | |
| **1b** [f] | 1901 [a] | 1 | 105.7 | 3,4 | 3.90–4.13(m) | 87.8 |
| | 1845 | 2 | 83.0 | 5 | 4.38(qd) | |
| | | 3–6 | 94.0 | 6 | 5.54(dq) | |
| | | | 93.1 | $CO_2Me$ | 3.28(s) | |
| | | | 90.9 | Me | 2.21(s) | |
| | | | 87.3 | | | |
| | | 7 | 168.2 | | | |
| | | 8 | 51.7 | | | |
| | | 9 | 21.4 | | | |
| | | CO | 239.1(20.5) | | | |
| | | | 238.6(20.5) | | | |
| **1c** [g] | 1901 [b] | 1 | 104.9 | 3 | 3.87(d) | 87.3 |
| | 1851 | 2 | 82.7 | 4 | 3.43(t) | |
| | | 3–6 | 95.2 | 5 | 4.51(m) | |
| | | | 94.1 | 6 | 5.67(qd) | |
| | | | 89.5 | $CO_2Me$ | 3.44(s) | |
| | | | 87.8 | Me | 2.46(s) | |
| | | 7 | 168.7 | | | |
| | | 8 | 51.9 | | | |
| | | 9 | 20.2 | | | |
| | | CO | 240.2(19.6) | | | |
| | | | 239.7(20.5) | | | |
| **1d** | 1901 [b] | 1 | 106.6 | 3 | 3.42(d) | 87.4 |
| | 1851 | 2 | 83.1 | 4 | 3.84(t) | |
| | | 3–6 | 95.1 | 5 | 4.39(m) | |
| | | | 94.0 | 6 | 5.47(qd) | |
| | | | 90.8 | $CO_2Me$ | 3.26(s) | |
| | | | 86.7 | Me | 2.49(s) | |
| | | 7 | 168.1 | | | |
| | | 8 | 51.6 | | | |
| | | 9 | 20.0 | | | |
| | | CO | 240.3(21.3) | | | |
| | | | 239.9(19.6) | | | |
| **2a** | 1976 [a] | 1 | 106.7 | 2 | 5.56(s) | |
| | 1902 | 3 | h | 4,5 | 4.31(m) | |
| | | 2,4–6 | 94.6 | 6 | 5.46(m) | |
| | | | 94.1 | $CO_2Me$ | 3.34(s) | |
| | | | 91.7 | Me | 1.41(s) | |
| | | | 91.1 | | | |
| | | 7 | 166.4 | | | |
| | | 8 | 52.9 | | | |
| | | 9 | 20.6 | | | |
| | | CO | 231.4 | | | |

Table 1 (continued)

| Complex | Infrared (cm$^{-1}$) | $^{13}$C NMR (ppm) [c] | | $^{1}$H NMR (ppm) [d] | | $^{31}$P NMR (ppm) [e] |
|---|---|---|---|---|---|---|
| **2b** | 1899 [a] | 1 | 102.4 | 2 | 5.46(s) | 86.8 |
| | 1841 | 3 | 86.0 | 4,5 | 4.08(m) | |
| | | 2,4–6 | 92.7 | 6 | 5.38(m) | |
| | | | 90.9 | $CO_2Me$ | 3.44(s) | |
| | | | 90.5 | Me | 1.77(s) | |
| | | | 88.1 | | | |
| | | 7 | 168.7 | | | |
| | | 8 | 52.1 | | | |
| | | 9 | 20.3 | | | |
| | | CO | 239.5(21.5) | | | |
| | | | 239.3(20.5) | | | |
| **2c** | 1900 [b] | 1 | 99.4 | 2,6 | 5.51(m) | 85.9 |
| | 1850 | 3 | 84.8 | 5 | 3.48(m) | |
| | | 2,4–6 | 93.8 | 4 | 4.45(d) | |
| | | | 93.1 | $CO_2Me$ | 3.51(s) | |
| | | | 90.8 | Me | 1.66(s) | |
| | | | 89.4 | | | |
| | | 7 | 168.5 | | | |
| | | 8 | 52.0 | | | |
| | | 9 | 20.1 | | | |
| | | CO | 240.6(18.6) | | | |
| | | | 239.8(20.5) | | | |
| **2d** | 1900 [b] | 1 | 101.9 | 2,6 | 5.46(s,br) | 85.8 |
| | 1850 | 3 | 85.5 | 4,5 | 3.80–3.90(m) | |
| | | 2,4–6 | 94.3 | $CO_2Me$ | 3.49(s) | |
| | | | 91.9 | Me | 1.51(s) | |
| | | | 90.2 | | | |
| | | | 88.6 | | | |
| | | 7 | 168.8 | | | |
| | | 8 | 52.0 | | | |
| | | 9 | 20.0 | | | |
| | | CO | 240.7(18.6) | | | |
| | | | 240.2(19.6) | | | |

[a] $CH_2Cl_2$ solution. [b] Petroleum ether (40–60) solution. [c] $CDCl_3$ solution, ppm from TMS; $J$(P–C) in parentheses. [d] $C_6D_6$ solution, ppm from TMS. [e] $CDCl_3$ solution, ppm from 85% $H_3PO_4$. [f] $PPh_3$ resonances: $^1$H: 6.94–7.67 ppm; $^{13}$C: 127.6–139.4 ppm; complex **2b** is similar. [g] NMDPP resonances: $^1$H-Me, 0.30(d,$J$ 7 Hz), CH$Me_2$, 1.20, 1.13(d,$J$ 6.3 Hz), 1.5–3.0(m), 6.9–7.9 (m) ppm; $^{13}$C ($C_{10}H_{19}$), 17.8, 21.0(12), 21.5, 23.9, 28.2(5.5), 28.7, 30.1, 30.9, 38.1(15.5), 39.7; Ph, 127–144 ppm; other NMDPP complexes are similar. [h] Not seen and coincident with one of resonances due to C2,4–6

CSe, $PF_3$) [18a–18c] or *anti* ($L = PPh_3$) [19] to the carboxylate carbonyl. In the present case, the phosphine is *trans* to the carboxylate, probably for steric reasons. The structure is otherwise unremarkable (Table 2) with an essentially coplanar $CO_2Me$ group [19,20], bond angles close to the octahedral values, an average Cr–arene bond length (2.203 Å) similar to those in (methylbenzoate)Cr$(CO)_2PPh_3$ (2.198 Å) [19] and (methylbenzoate)Cr$(CO)_3$ (2.219 Å) [20], and a Cr–P bond length similar to those in other (arene)Cr$(CO)_2PPh_3$ complexes [19,21a–21c].

With respect to reactivity, it is known that phosphine substitution decreases the susceptibility of the ring to nucleophilic attack, but does not prohibit carbon–carbon bond forming reactions involving simple carbon nucleophiles [12a*]. In the absence of strongly directing arene substituents, the regiospecificity of nucleophilic attack in

*(continued on p. 58)*

Table 2

Structural data for (1d)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *(a) Bond lengths (Å)* | | | | | | | |
| Cr1–P1 | 2.334(5) | Cr1–C1 | 1.828(18) | C7–C8 | 1.380(23) | C12–C13 | 1.417(20) |
| Cr1–C2 | 1.763(18) | Cr1–C3 | 2.179(17) | C12–C17 | 1.387(20) | C13–C14 | 1.338(24) |
| Cr1–C4 | 2.222(17) | Cr1–C5 | 2.237(21) | C14–C15 | 1.393(24) | C15–C16 | 1.374(23) |
| Cr1–C6 | 2.209(19) | Cr1–C7 | 2.193(18) | C16–C17 | 1.366(22) | C18–C19 | 1.388(23) |
| Cr1–C8 | 2.180(17) | P1–C12 | 1.873(15) | C18–C23 | 1.400(20) | C19–C20 | 1.413(22) |
| P1–C18 | 1.797(16) | P1–C24 | 1.854(16) | C20–C21 | 1.420(23) | C21–C22 | 1.342(23) |
| O1–C1 | 1.165(17) | O2–C2 | 1.189(18) | C22–C23 | 1.371(22) | C24–C25 | 1.554(21) |
| O3–C10 | 1.140(22) | O4–C10 | 1.341(24) | C24–C29 | 1.586(21) | C25–C26 | 1.51(3) |
| O4–C11 | 1.424(22) | C3–C4 | 1.415(23) | C25–C30 | 1.615(24) | C26–C27 | 1.60(3) |
| C3–C8 | 1.457(23) | C3–C10 | 1.532(25) | C27–C28 | 1.49(3) | C28–C29 | 1.520(24) |
| C4–C5 | 1.409(23) | C4–C9 | 1.504(23) | C28–C33 | 1.58(3) | C30–C31 | 1.50(3) |
| C5–C6 | 1.394(25) | C6–C7 | 1.355(24) | | | | |
| *(b) Bond angles (degrees)* | | | | | | | |
| C1–Cr1–P1 | 87.8(6) | C2–Cr1–P1 | 94.0(6) | C5–C4–Cr1 | 72(1) | C5–C4–C3 | 120(2) |
| C2–Cr1–C1 | 89.0(7) | C3–Cr1–P1 | 161.3(5) | C9–C4–Cr1 | 130(1) | C9–C4–C3 | 124(2) |
| C3–Cr1–C1 | 94.3(7) | C3–Cr1–C2 | 104.7(8) | C9–C4–C5 | 116(2) | C4–C5–Cr1 | 71(1) |
| C4–Cr1–P1 | 124.3(5) | C4–Cr1–C1 | 86.9(7) | C6–C5–Cr1 | 71(1) | C6–C5–C4 | 120(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C4–Cr1–C2 | 141.2(8) | C4–Cr1–C3 | 37.5(6) | C5–C6–Cr1 | 73(1) | C7–C6–Cr1 | 71(1) |
| C5–Cr1–P1 | 94.4(5) | C5–Cr1–C1 | 108.0(7) | C7–C6–C5 | 122(2) | C6–C7–Cr1 | 73(1) |
| C5–Cr1–C2 | 161.3(8) | C5–Cr1–C3 | 67.2(7) | C8–C7–Cr1 | 71(1) | C8–C7–C6 | 120(2) |
| C5–Cr1–C4 | 36.8(6) | C6–Cr1–P1 | 87.7(5) | C3–C8–Cr1 | 70(1) | C7–C8–Cr1 | 72(1) |
| C6–Cr1–C1 | 143.6(7) | C6–Cr1–C2 | 127.4(8) | C7–C8–C3 | 121(2) | O4–C10–O3 | 128(2) |
| C6–Cr1–C3 | 79.6(7) | C6–Cr1–C4 | 66.4(7) | C3–C10–O3 | 124(2) | C3–C10–O4 | 108(2) |
| C6–Cr1–C5 | 36.5(6) | C7–Cr1–P1 | 108.1(5) | C13–C12–P1 | 122(1) | C17–C12–P1 | 117(1) |
| C7–Cr1–C1 | 162.9(7) | C7–Cr1–C2 | 95.8(8) | C17–C12–C13 | 120(1) | C14–C13–C12 | 119(2) |
| C7–Cr1–C3 | 68.6(7) | C7–Cr1–C4 | 79.1(7) | C15–C14–C13 | 119(2) | C16–C15–C14 | 122(2) |
| C7–Cr1–C5 | 65.7(7) | C7–Cr1–C6 | 35.8(6) | C17–C16–C15 | 118(2) | C16–C17–C12 | 120(1) |
| C8–Cr1–P1 | 144.0(4) | C8–Cr1–C1 | 128.0(7) | C19–C18–P1 | 118(1) | C23–C18–P1 | 126(1) |
| C8–Cr1–C2 | 85.1(7) | C8–Cr1–C3 | 39.1(6) | C23–C18–C19 | 115(1) | C20–C19–C18 | 123(2) |
| C8–Cr1–C4 | 67.8(6) | C8–Cr1–C5 | 78.3(7) | C21–C20–C19 | 118(2) | C22–C21–C20 | 119(2) |
| C8–Cr1–C6 | 65.4(7) | C8–Cr1–C7 | 36.8(6) | C23–C22–C21 | 121(2) | C22–C23–C18 | 123(2) |
| C12–P1–Cr1 | 118.6(5) | C18–P1–Cr1 | 109.9(5) | C25–C24–P1 | 117(1) | C29–C24–P1 | 116(1) |
| C18–P1–C12 | 102.5(7) | C24–P1–Cr1 | 117.7(5) | C29–C24–C25 | 111(1) | C26–C25–C24 | 111(1) |
| C24–P1–C12 | 106.4(7) | C24–P1–C18 | 99.0(7) | C30–C25–C24 | 117(1) | C30–C25–C26 | 116(2) |
| C11–O4–C10 | 113(2) | O1–C1–Cr1 | 176(2) | C27–C26–C25 | 114(2) | C28–C27–C26 | 112(2) |
| O2–C2–Cr1 | 175(2) | C4–C3–Cr1 | 73(1) | C29–C28–C27 | 113(2) | C33–C28–C27 | 112(2) |
| C8–C3–Cr1 | 70(1) | C8–C3–C4 | 117(1) | C33–C28–C29 | 113(2) | C28–C29–C24 | 109(1) |
| C10–C3–Cr1 | 130(1) | C10–C3–C4 | 123(2) | C31–C30–C25 | 115(2) | C32–C30–C25 | 112(2) |
| C10–C3–C8 | 120(2) | C3–C4–Cr1 | 70(1) | C32–C30–C31 | 110(2) | | |

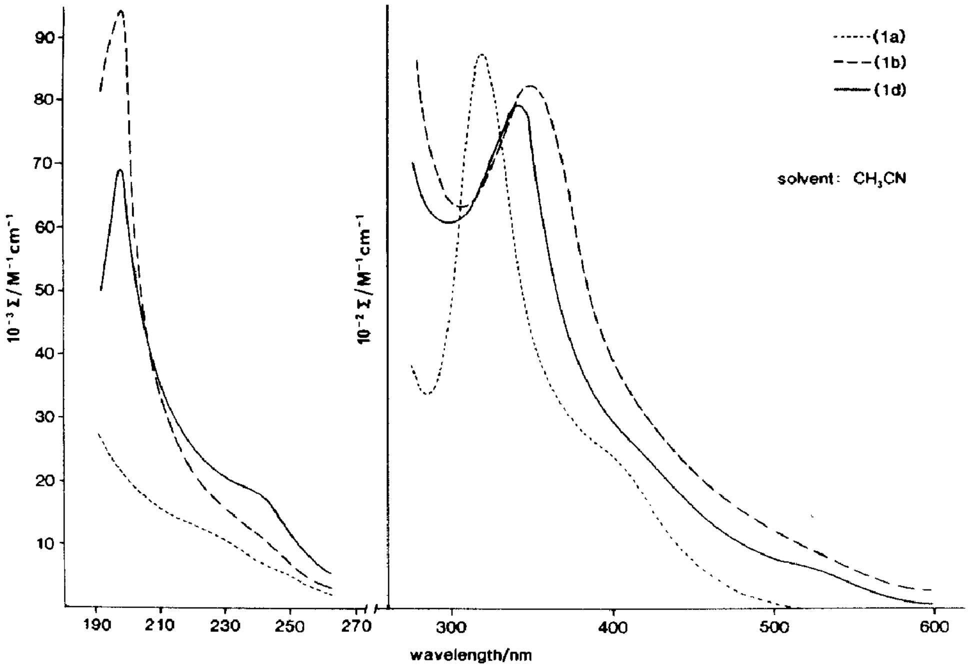


Fig. 2. UV/visible spectra of complexes **1a**, **1b**, **1d**.

substituted complexes is determined by the orientation of the $Cr(CO)_3$ moiety relative to the ring [21]. To our knowledge, the effects of phosphine substitution on regioselectivity have not been examined, though changes both in the orientation of the $Cr(CO)_2L$ moiety and in the stereochemistry of arene substituents in sterically crowded molecules have been observed [21b].

The absolute planar configurations of **2c**, **2d** have been assigned as shown by conversion of a sample of **2a** containing a 76% e.e. of the (−)-(1*S*) enantiomer [23*,24] to a mixture of **2c**, **2d** which is enriched to the same extent in **2d**. We have also assessed the utility of CD spectroscopy in the assignment of absolute configurations, since in the (diene)$Fe(CO)_2L$ series (L = CO, phosphine), both we [11a,11b] and others [25a,25b] have shown that for closely related complexes, the sign of the CD absorption associated with the longest wavelength UV/visible absorptions may be used to assign absolute configuration. In particular, the CD spectra of separated diastereoisomers of the type (diene)$Fe(CO)_2$(NMDPP) are essentially mirror image in this region, and bear a close similarity to the tricarbonyl of the same planar chirality.

Though there are some uncertainties in the literature [26a–26f], the UV/visible spectrum of **1a** (Fig. 2) [27*] may be assigned as (a) 320 nm with shoulder at 400 nm, metal–arene charge transfer, possibly overlying ligand field transitions and (b) 225 nm with shoulder at 250 nm, metal–CO and (metal–arene)–CO charge transfer. Phosphine substitution to give **1b** or **1d** results in a substantial bathochromic shift, and the appearance of a high intensity band at 195 nm that is obscured by the solvent cut-off for **1a** but appears in gas phase spectra [28] of (arene)$Cr(CO)_3$ complexes, and is assigned to (metal-arene)–CO charge transfer with a substantial contribution from arene substituent atomic orbitals. The UV/visible spectra of **2a**–**2d** show a similar relationship, with those of **2c**, **2d** being superposable.

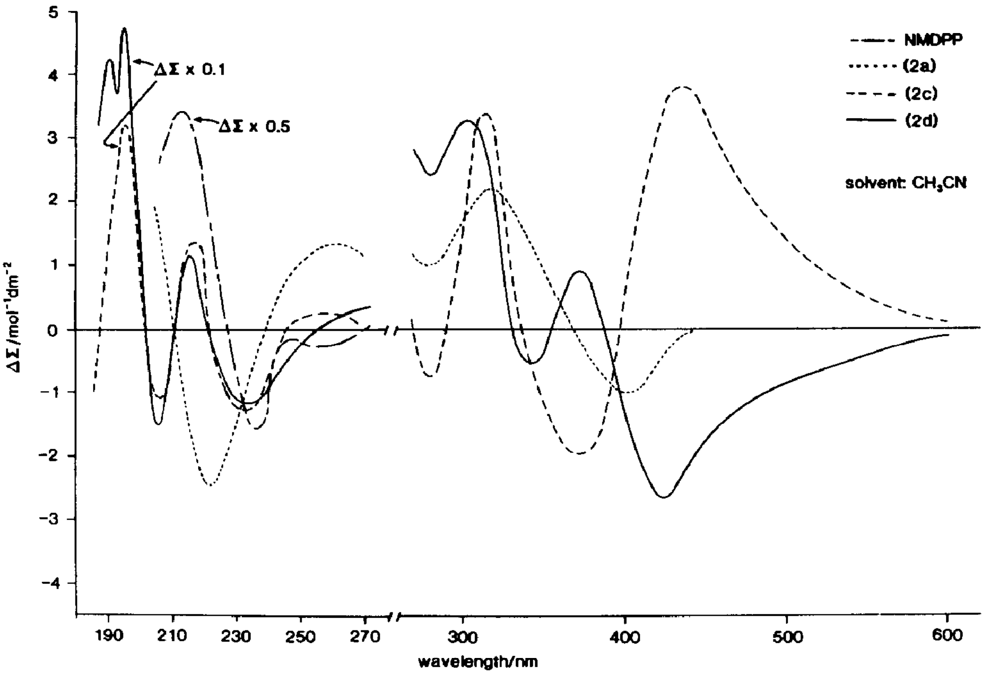


Fig. 3. CD spectra of NMDPP and complexes **2a**, **2c**, **2d**.

The CD spectra of **2c**, **2d** (Fig. 3) do show an approximate mirror image in the region associated with the longest wavelength transition, and have the correct relationship to the sign of the longest wavelength transition of the (−)-(1*S*)

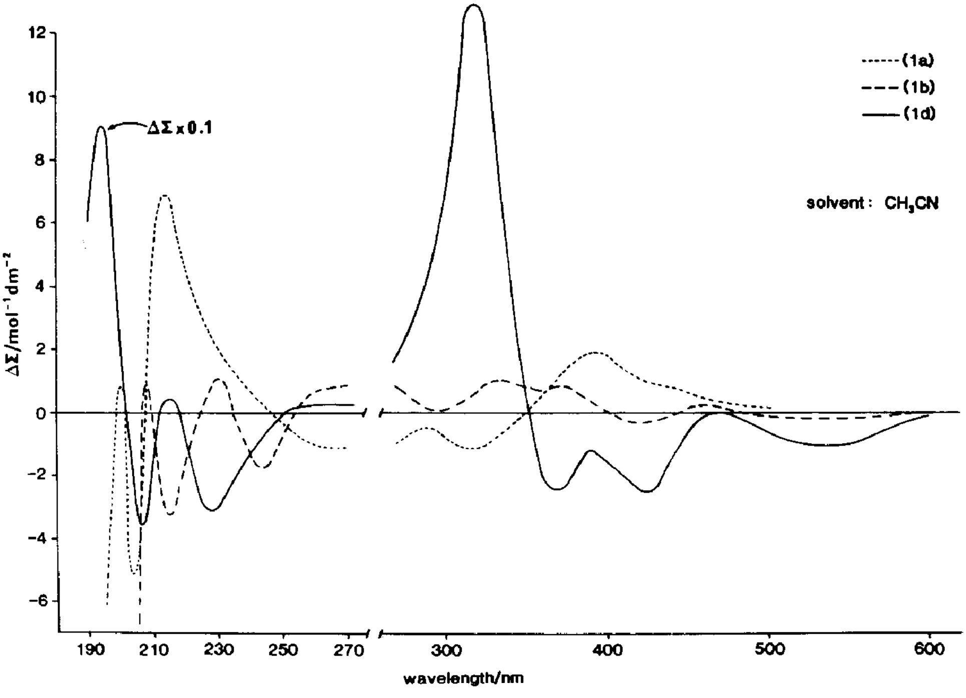


Fig. 4. CD spectra of complexes **1a**, **1b**, **1d**.

tricarbonyl [23*] in this region. Unusually, however, the spectra of **2c**, **2d** and of **1d** (Fig. 4) are almost superposable in the region below 320 nm, except for a reversal in sign for **2c**, **2d** associated with the highest energy transition at 190 nm. The CD bands are also approximately ten times more intense than those of the tricarbonyls in this region, a feature that can be attributed partly to significant absorption by NMDPP itself (Fig. 3) and partly to a substantial induction in chirality by NMDPP in the complex bands which masks the opposing planar chirality. Even at longer wavelength, the CD spectra of **1a** and **1d** (having the same (1*S*) planar configuration) have no simple relationship (Fig. 4). Spectral changes here appear to result simply from phosphine substitution, since the spectrum of **1b** [23*] in this region parallels that of **1d**, although of lower intensity. One other example of a substantial change in the CD spectrum on $PPh_3$ substitution has been reported [29]; the origin is unclear, but may perhaps be associated with different conformational energy minima for the $Cr(CO)_3$ and $Cr(CO)_2PPh_3$ complexes. Thus, the assignment of absolute configuration of metal-substituted (arene)$Cr(CO)_3$ complexes based on CD spectroscopy must be approached with caution.

We are currently examining synthetic applications of this approach.

## Experimental

NMR, infrared and UV/visible spectra were recorded on a JEOL FX-100, a Perkin–Elmer 257 and a Pye Unicam SP8-100 spectrometer, respectively. Solvents were dried and degassed before use, and all reactions were conducted under nitrogen. Published methods were used to prepare (*ortho*- and (*meta*-$MeC_6H_4CO_2Me$)$Cr(CO)_3$ [31] and NMDPP [32]. The phosphine used contained about 10% of the phosphine oxide as an impurity.

### *(a) Preparation and diastereoisomer separation*

A mixture of 2 g (6.99 mmol) of (*meta*-$MeC_6H_4CO_2Me$)$Cr(CO)_3$ (**2a**) and 3.4 g (10.5 mmol) of NMDPP in benzene (270 ml) was irradiated with a 120 W medium pressure mercury lamp with continuous $N_2$ flushing until the IR spectrum of a sample indicated disappearance of the starting material (ca. 3 h). The solvent was removed under vacuum and the residue was dissolved in acetone (30 ml) containing MeI (5 ml). After 30 min stirring, the solvent and excess MeI were removed under vacuum, the residue was extracted with diethyl ether, and chromatographed on silica with diethyl ether as eluant. Solvent was removed from the single red band to give the product **2c**, **2d** (3.25 g, 80%) as a red oil. Accurate mass ($M^+$) found: 582. 1963 (calc.: 582.1981).

The diastereoisomer mixture was separated on a 500 mg scale on 2 mm Chromatotron plates using 1% ethyl acetate/petroleum ether (b.p. 40–60 °C) as eluant. Two distinct orange-red bands were collected, to yield **2c** and **2d** as red oils in order of elution.

(*ortho*-$MeC_6H_4CO_2Me$)$Cr(CO)_2$(NMDPP) was prepared similarly (86%) and separated on the Chromatotron with 2% ethyl acetate/petroleum ether (b.p. 40–60 °C) as eluant to give **1c** as a red oil and **1d** as red crystals in order of elution; **1d** was recrystallised from petroleum ether (b.p. 60–80 °C). Analysis: C, 68.0(68.0), H, 6.71(6.70). M.p. 181–182 °C.

(*meta*-MeC$_6$H$_4$CO$_2$Me)Cr(CO)$_2$PPh$_3$ (**2b**) (82%) and (*ortho*-MeC$_6$H$_4$CO$_2$Me) Cr(CO)$_2$PPh$_3$ (**1b**) (65%) were prepared similarly and recrystallized from ethylacetate/petroleum ether (b.p. 60–80 °C). Analysis: C, 66.8 (66.9); H, 4.85 (4.81) (**2b**). M.p. 155–156 °C. C, 66.8 (66.9); H, 4.76 (4.81) (**1b**). M.p. 144–145 °C.

### *(b) Crystal structure determination of **1d***

A crystal of approximate dimensions 0.1 × 0.1 × 0.32 mm was used for data collection on an Enraf–Nonius CAD4F diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å) and a graphite monochromator in the range $2 < \theta < 24°$.

Table 3

Fractional atomic coordinates for **1d**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cr1 | −0.2264(2) | −0.9688(2) | −0.9088(2) |
| P1 | −0.0793(3) | −1.0535(3) | −0.9291(2) |
| O1 | −0.3191(9) | −1.0712(9) | −1.0549(8) |
| O2 | −0.3175(10) | −1.0999(10) | −0.7869(9) |
| O3 | −0.4865(12) | −0.8382(10) | −0.9939(11) |
| O4 | −0.4949(12) | −0.8915(11) | −0.8604(10) |
| C1 | −0.2811(13) | −1.0340(12) | −0.9973(10) |
| C2 | −0.2785(14) | −1.0501(12) | −0.8374(11) |
| C3 | −0.3368(12) | −0.8576(12) | −0.9152(12) |
| C4 | −0.2660(15) | −0.8413(11) | −0.9809(12) |
| C5 | −0.1631(15) | −0.8370(13) | −0.9612(13) |
| C6 | −0.1313(15) | −0.8482(12) | −0.8771(13) |
| C7 | −0.1970(13) | −0.8619(12) | −0.8124(12) |
| C8 | −0.2987(12) | −0.8652(11) | −0.8283(11) |
| C9 | −0.2938(14) | −0.8291(13) | −1.0732(11) |
| C10 | −0.4498(16) | −0.8617(15) | −0.9319(15) |
| C11 | −0.6014(17) | −0.8881(19) | −0.8655(16) |
| C12 | 0.0080(11) | −1.0689(10) | −0.8365(10) |
| C13 | 0.1089(13) | −1.0973(12) | −0.8469(11) |
| C14 | 0.1642(16) | −1.1155(14) | −0.7777(13) |
| C15 | 0.1233(15) | −1.1014(13) | −0.6969(13) |
| C16 | 0.0266(13) | −1.0713(12) | −0.6850(12) |
| C17 | −0.0307(12) | −1.0538(11) | −0.7554(10) |
| C18 | −0.0012(12) | −0.9966(10) | −1.0065(10) |
| C19 | −0.0329(11) | −0.9940(11) | −1.0908(11) |
| C20 | 0.0174(13) | −0.9427(13) | −1.1546(12) |
| C21 | 0.1012(15) | −0.8881(14) | −1.1302(13) |
| C22 | 0.1323(14) | −0.8906(13) | −1.0488(12) |
| C23 | 0.0818(12) | −0.9406(11) | −0.9881(11) |
| C24 | −0.0898(11) | −1.1686(11) | −0.9811(10) |
| C25 | −0.1623(14) | −1.2401(12) | −0.9401(11) |
| C26 | −0.1776(16) | −1.3224(15) | −0.9980(14) |
| C27 | −0.0759(17) | −1.3669(16) | −1.0330(15) |
| C28 | −0.0070(16) | −1.2955(14) | −1.0679(13) |
| C29 | 0.0132(12) | −1.2162(10) | −1.0063(11) |
| C30 | −0.1471(14) | −1.2634(15) | −0.8401(12) |
| C31 | −0.0489(17) | −1.3083(17) | −0.8177(15) |
| C32 | −0.2325(18) | −1.3189(16) | −0.8049(15) |
| C33 | −0.0414(17) | −1.2618(16) | −1.1591(13) |

Crystal data: orthorhombic, $a$ 13.338(2), $b$ 14.420(4), $c$ 15.668(5) Å, $U$ 3013.49 Å$^3$, $\mu$ 5.38 cm$^{-1}$, $F(000) = 1216$, space group $P2_12_12_1$, $Z = 4$.

The structure was solved by a combination of Patterson search and direct methods (SHELX86) [33] and refined by full matrix least squares (SHELX76) [34]. Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The chromium and phosphorus atoms were refined anisotropically. Atomic scattering factors for non-hydrogen and hydrogen atoms and anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [35a–35c]. All calculations were performed on a VAX 8700 computer; the ORTEP program [36] was used to give the drawings.

Final full matrix least squares cycle: 951 reflections with $I > 2\sigma I$, 167 variable parameters, maximum shift/ESD < 0.001, residuals $R$ 5.70, $R_w$ 6.00%. Final difference Fourier map: maximum peak 0.13 e/Å$^3$, minimum peak 0.10 e/Å$^3$. Refinement with inversion of absolute planar chirality and neomenthyl chirality gave $R$ 5.97, $R_w$ 6.27%.

A list of fractional atomic coordinates is given in Table 3. Tables of hydrogen atom-coordinates, thermal parameters, and observed and calculated structure factors are available from the authors.

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## References

1 For reviews, see (a) G. Jaouen, Pure Appl. Chem., 58 (1986) 597; (b) E.P. Kundig, Pure Appl. Chem., 57 (1985) 1855; (c) M.F. Semmelhack, G.R. Clark, J.L. Harrison, Y. Thebtaranonth, J.L. Garcia, A. Wulff, and A. Yamashita, Tetrahedron, 37 (1981) 3957.

2 For recent work, see (a) P.J. Dickens, A.Z.M. Slawin, D.A. Widdowson, and D.J. Williams, Tetrahedron Lett., 29 (1988) 103; (b) J. Blagg, S.G. Davies, C.L. Goodfellow and K.H. Sutton, J. Chem. Soc., Perkin Trans. I, (1987) 1805; (c) J.A. Heppert, M.E. Thomas-Miller, P.N. Swepston and M.W. Extine, J. Chem. Soc., Chem. Comm., (1988) 280; (d) J.L. Davidson, H. Patel and P.N. Preston, J. Organomet. Chem., 336 (1987) C44; (e) E.P. Kundig, C. Grivet and S. Spichiger, ibid., 332 (1987) C13.

3 For recent work, see (a) R.C. Cambie, G.R. Clark, S.R. Gallagher, P.S. Rutledge, M.J. Stone and P.D. Woodgate, J. Organomet. Chem., 348 (1988) 317; (b) B. Ohlsson and C. Ullenius, ibid., 350 (1988) 35; (c) H. Kunzer and M. Thiel, Tetrahedron Lett., 29 (1988) 3223; (d) R.D. Rieke and K.P. Darawala, J. Org. Chem., 53 (1988) 2073.

4 For recent work, see (a) J.Y. Le Bihan, M.C. Senechal-Tocquer, D. Senechal, D. Gentric, B. Caro, J.F. Halet, J.Y. Saillard, G. Jaouen and S. Top, Tetrahedron, 44 (1988) 3565; (b) J. Blagg, S.J. Coote, S.G. Davies, D. Middlemiss and A. Naylor, J. Chem. Soc., Perkin Trans. I, (1987) 689; (c) S.J. Coote, S.G. Davies and K.H. Sutton, J. Chem. Soc., Perkin Trans. I, (1988) 1481; (d) D. Senechal, M.C. Senechal-Tocquer, D. Gentric, J.Y. Le Bihan, B. Carol, M. Gruselle and G. Jaouen, J. Chem. Soc., Chem. Comm., (1987) 632.

5 For recent work, see (a) C. Baldoli, P. del Buttero, E. Licandro, S. Maiorana and A. Papagni, J. Chem. Soc., Chem. Comm., (1987) 762; (b) A. Solladie-Cavallo, G. Lapitajs, P. Buchert, A. Klein, S. Colonna and A. Manfredi, J. Organomet. Chem., 330 (1987) 357; (c) J. Brocard, L. Pelinski and J. Lebibi, ibid., 337 (1987) C47.

6 R.M. Moriarty, S.C. Engerer, O. Prakash, I. Prakash, U.S. Gill and W.A. Freeman, J. Org. Chem., 52 (1987) 153.

7 (a) H. Falk, K. Schogl and W. Steyrer, Monatsh. Chem., 97 (1967) 1029; (b) R. Dabard, A. Meyer and G. Jaouen, C.R. Acad. Sc. Paris, Ser. C., 268 (1969) 201; (c) A. Meyer, Ann. Chim., 8 (1973) 397; (d) G. Jaouen and A. Meyer, J. Am. Chem. Soc., 97 (1975) 4667; (e) A. Solladie-Cavallo, G. Solladie and E. Tsamo, Inorg. Synth., 23 (1985) 85.

8 K.R. Stewart, S.G. Levine and J. Bordner, J. Org. Chem., 49 (1984) 4082.

9 For potentially useful diastereoselective complexations in racemic series, see (a) M. Uemura, T. Minami and Y. Hayashi, J. Am. Chem. Soc., 109 (1987) 5277; (b) J. Brocard, J. Lebibi, L. Pelinski and M. Mahmoudi, Tetrahedron Lett., 27 (1986) 6325; (c) S.G. Davies and C.L. Goodfellow, J. Organomet. Chem., 340 (1988) 195.

10 J. Gillois, D. Buisson, R. Azerad and G. Jaouen, J. Chem. Soc., Chem. Comm., (1988) 1224.

11 (a) J.A.S. Howell, A.D. Squibb, G. Walton, P. McArdle and D. Cunningham, J. Organomet. Chem., 319 (1987) C45; (b) J.A.S. Howell, M.C. Tirvengadum, A.D. Squibb, G. Walton, P. McArdle and D. Cunningham, ibid., 347 (1988) C5.

12 For similar photolytic preparations, see (a) M.F. Semmelhack, W. Seufert and L. Keller, J. Organomet. Chem., 226 (1982) 183; (b) M. Cais, M. Kaftory, D.H. Kohn and D. Tatarsky, ibid., 184 (1979) 103; (c) G. Jaouen and R. Dabard, ibid., 72 (1974) 377; (d) W.R. Jackson, C.F. Pincombe, I.D. Rae, D. Rash and B. Wilkinson, Aust. J. Chem., 29 (1976) 2431.

13 For recent work, see (a) M. Nambu and J.S. Siegel, J. Am. Chem. Soc., 110 (1988) 3675; (b) X. Hu, J. Duchowski and R.K. Pomeroy, J. Chem. Soc., Chem. Comm., (1988) 362.

14 Such effects can dominate the preferred conformation: (a) F. van Meurs and H. Konigsfeld, J. Organomet. Chem., 118 (1976) 295; (b) idem, ibid., 131 (1977) 423; (c) idem, ibid., 78 (1974) 229; (d) F. van Meurs and J.M. van der Toorn, ibid., 113 (1976) 341.

15 (a) Y. Dusausoy, J. Protas, J. Besancon and J. Tirouflet, Acta Cryst. B, 29 (1973) 469; (b) Y. Dusausoy, J. Protas, J. Besancon and J. Tirouflet, Acta Cryst. B, 28 (1972) 3183; (c) F. Baert, J. Lamot, J. Lebibi and J. Brocard, Acta Cryst. C, 44 (1988) 1389.

16 (a) R. Mercier and J. Vebrel, Acta Cryst. B, 37 (1981) 1071; (b) J.C. Boutonnet, J. Levisalles, F. Rose, G. Precigoux, C. Courselle and N. Plazter, J. Organomet. Chem., 255 (1983) 317; (c) J.C. Boutonnet, J. Levisalles, F. Rose-Munch and E. Rose, ibid., 290 (1985) 153; (d) P. Berno, A. Ceccon, F. Dapra, A. Gambaro, A. Venzo, P. Ganis and G. Vall, ibid., 301 (1986) 161; (e) V. Kunz and W. Nowacki, Helv. Chim. Acta, 50 (1967) 1052.

17 P. Le Maux, G. Simmoneux, G. Jaouen, L. Ouhab and P. Batail, J. Am. Chem. Soc., 100 (1978) 4312.

18 (a) J.Y. Saillard, D. Grandjean, A. Le Beuze and G. Simmoneaux, J. Organomet. Chem., 204 (1981) 197; (b) J.Y. Saillard, G. Le Borgne and D. Grandjean, ibid., 94 (1975) 409.

19 V.G. Andrianov, Y.T. Struchkov, W.K. Baranetskaya, V.N. Setkina and D.N. Kursanov, J. Organomet. Chem., 101 (1975) 209.

20 J.Y. Saillard and D. Grandjean, Acta Cryst. B, 32 (1976) 2285.

21 (a) M. Kaftory, Acta Cryst., B, 36 (1980) 2971; (b) D.J. Iverson, G. Hunter, J.F. Blount, J.R. Damewood and K. Mislow, J. Am. Chem. Soc., 103 (1981) 6073; (c) E.M. Campi, B.M.K. Gatehouse, W.R. Jackson, I.D. Rae and M.G. Wong, Can. J. Chem., 62 (1984) 2566.

22 T.A. Albright and B.K. Carpenter, Inorg. Chem., 19 (1980) 3092.

23 Samples of (+)-(1*S*)-**1a** and (−)-(1*S*)-**2a** of 82 and 76% e.e. were obtained by fractional crystallization of the (−)-$\alpha$-phenylethylamine salts of $(MeC_6H_4CO_2H)Cr(CO)_3$ followed by reconversion to the acid and reaction with $CH_2N_2$ [7a]. Photolytic substitution of **1a** above yielded (after one recrystallization) a sample of **1b** of 89% e.e.. The e.e. may easily be assessed by proton NMR in the presence of tris{3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) using the $CO_2Me$ resonance for **2a** and the ring methyl resonance for **1a**, **1b**. CD spectra of **1a**, **1b** and **2a** in Fig. 3 and 4 have been corrected to show spectra of optically pure materials; CD spectra of **1a** and **2a** are essentially the same as those reported previously in solvents of higher cut-off [7c,30].

24 M.A. Bush, T.A. Dullforce and G.A. Sim, J. Chem. Soc., Chem. Comm., (1969) 1491.

25 See, for example, (a) N.W. Alcock, D.H.G. Crout, C.M. Henderson and S.E. Thomas, J. Chem. Soc., Chem. Comm., (1988) 746; (b) A. Tajiri, H. Sotokawa, N. Morita, C. Kabuto, M. Hatano and T. Asao, Tetrahedron Lett., 28 (1987) 6495.

26 (a) D.G. Carroll and S.P. McGlynn, Inorg. Chem., 7 (1968) 1285; (b) I.M. Baibich and I.S. Butler, Inorg. Chim. Acta, 89 (1984) 73; (c) G.A. Razuvaev, V.A. Kuznetsov, A.N. Egorochkin, A.A. Klimov, A.N. Artemov and N.I. Sirotkin, J. Organomet. Chem., 128 (1977) 213; (d) G.T.W. Wittmann, G.N. Krynauw, S. Lotz and W. Ludwig, ibid., 293 (1985) C33; (e) R. Schreiner and A.B. Ellis, J. Am. Chem. Soc., 104 (1982) 3374; (f) C.A.L. Mahaffy and J. Rawlings, Spectroscopy Lett., 19 (1986) 517.

27 We have assessed the possibility of solvent displacement of arene in **2a**, **2b** using NMR; for **2a**, ca. 5% of free arene can be detected after 8 h at room temperature; no arene displacement is apparent for **2b** under the same conditions.
28 D. Rooney, J. Chaiken and D. Driscoll, Inorg. Chem., 26 (1987) 3939.
29 K. Schlogl, A. Werner and M. Widholm, Monatsh. Chem., 117 (1986) 1423.
30 K. Schlogl and R. Schoelm, Liebigs Ann. Chem., (1980) 1877.
31 C.A.L. Mahaffy and P.L. Pauson, Inorg. Synth., 19 (1979) 154.
32 J.D. Morrison and W.F. Masher, J. Org. Chem. 39 (1974) 270.
33 G.M. Sheldrick, SHELX86, A Computer Program for Crystal Structure Determination, University of Gottingen, 1986.
34 G.M. Sheldrick, SHELX76, A Computer Program for Crystal Structure Determination, University of Cambridge, 1976.
35 (a) D.T. Cromer and J.B. Mann, Acta Cryst. A, 24 (1968) 321; (b) R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175; (c) D.T. Cromer and D.J. Liberman, ibid., 53 (1970) 1891.
36 C.K. Johnson, ORTEP, Oak Ridge Natl. Lab. (Rep) ORNL (US), 1965–3794 (revised 1971).