Pergamon

*Polyhedron* Vol. 14, No. 13-14, pp. 1765-1770, 1995

0277-5387/95 $9.50+0.00

0277-5387(94)00484-6

# PENTAMETHYLCYCLOPENTADIENYL RUTHENIUM COMPLEXES AS POTENTIAL OPTICALLY NON-LINEAR MATERIALS

**DUNCAN W. BRUCE*† and ANNA THORNTON**

Centre for Molecular Materials and Department of Chemistry, The University, Sheffield S3 7HF, U.K.

**and**

**BRUNO CHAUDRET* and SYLVIANE SABO-ETIENNE**

Laboratoire de Chimie de Coordination, CNRS, 205 route de Narbonne, 31077 Toulouse, France

**and**

**TONY L. AXON and GRAHAM H. CROSS**

Centre for Molecular Electronics, Department of Applied Physics, University of Durham, Durham, U.K.

(*Received* 25 *October* 1994; *accepted* 18 *November* 1994)

**Abstract**—Several alkoxystilbazole derivatives were $\pi$-bound to the $[Cp^*Ru]^+$ fragment and the resulting complexes were examined for potential second-order non-linear optical effects.

The search for good optically non-linear materials is driven by the desire to be able to process optical information efficiently and in this context, optically non-linear molecular species have attracted much attention because of their higher intrinsic non-linearities and their higher thresholds to laser damage. As part of this effort, various research teams have become interested in evaluating the properties of metal-based molecular species given the high and polarizable electron density which is a feature of metal complexes.[1] The effect that the inclusion of metals may have on the linear polarizabilities (and related properties) of liquid crystalline coordination compounds has already been described.[2]

Several ferrocene derivatives have been shown to be very efficient optically non-linear materials and molecular hyperpolarizabilities of up to $66 \times 10^{-30}$ esu[3] and solid state second harmonic generation (SHG) efficiencies of up to 220 × urea (at 1907 nm)[4] have been measured.

Related ruthenocene systems have also been studied[5,6] and while the increased energy of the HOMO–LUMO gap in these systems (as evidenced by colour and cyclic voltammetry) inevitably led to materials in which $\beta$ was lower than in the corresponding iron systems, this presented one potential advantage in that the high-energy shift in $\lambda_{max}$ led to greater transparency at 532 nm, opening up additional potential applications.

Some of us have recently shown the high affinity of the $[Cp^*Ru]^+$ fragment ($Cp^* = \eta^5$-$C_5Me_5$) for aromatic systems.[7] The moiety $[Cp^*Ru]^+$ was obtained by the reaction of $[Cp^*Ru(OCH_3)]_2$ and triflic acid; subsequent addition of molecules capable of $\pi$-bonding led to a large variety of complexes (Fig. 1).

Given the synthetic flexibility offered by such

*Authors to whom correspondence should be addressed.

†DWB is Sir Edward Frankland Fellow of the Royal Society of Chemistry, 1994–1995.

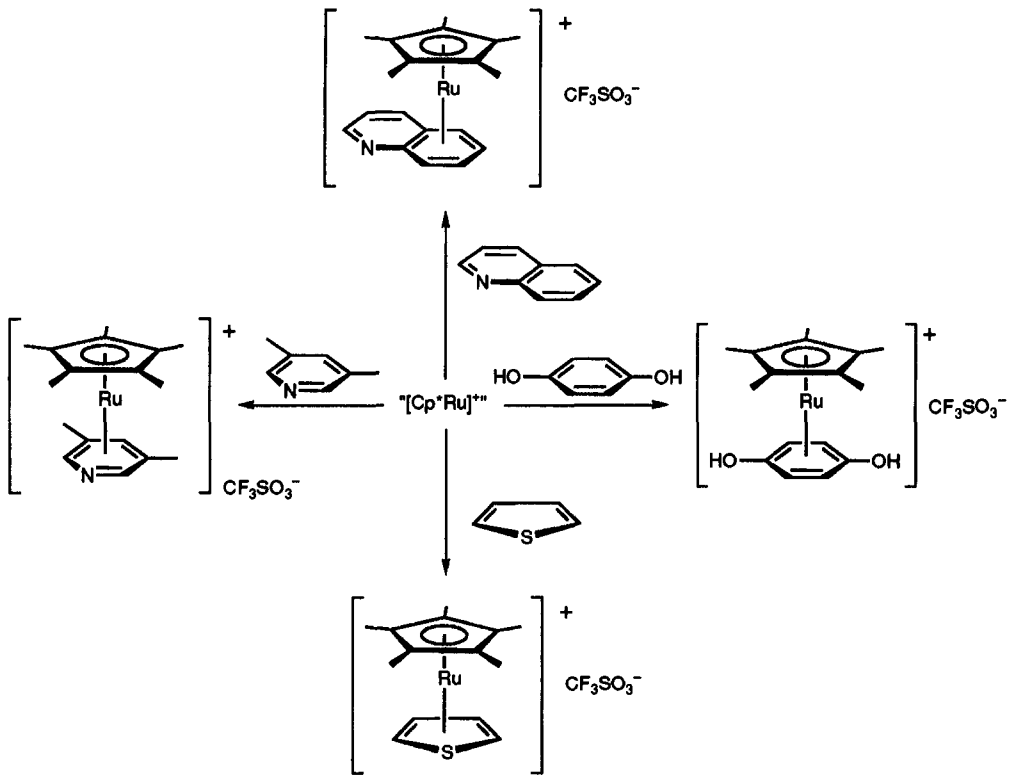



Fig. 1. Synthetic interconvertability of "[Cp*Ru]$^+$".

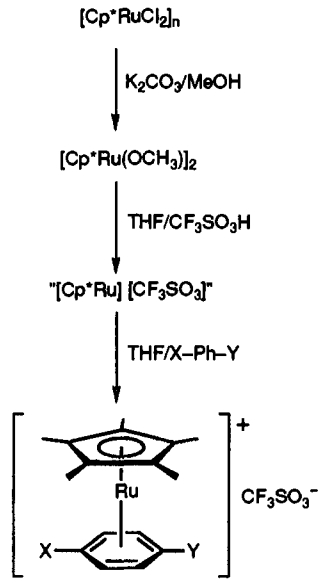
systems, we therefore undertook the synthesis of Cp*Ru complexes with $\pi$-bound stilbazole/derivatives as optically non-linear materials. Since the complexes were salts, we reasoned that this would promote non-centrosymmetry in the crystal packing.

## RESULTS AND DISCUSSION

### *Synthesis*

The complexes were synthesized as shown in Scheme 1.

A tetrahydrofuran (THF) solution of the $[Cp^*Ru]^+$ fragment, prepared *in situ* by addition of triflic acid to $[Cp^*Ru(OMe)]_2$ was immediately transferred into a degassed Fischer–Porter tube containing a solution of the chosen ligand in THF. The mixture was then heated at about 80–90°C at constant volume for about 48 h, after which the mixture was cooled and the solvent removed. The residue was washed with diethyl ether and pentane and the product was extracted with dichloromethane and crystallized.




Scheme 1. Scheme to illustrate the preparation of the new complexes.

### *Complex with* trans-4-*methoxystilbazole*

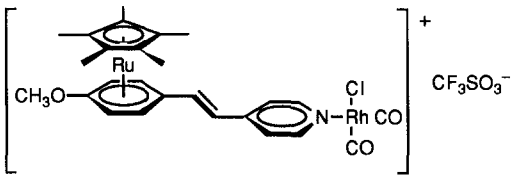
The first ligand was *trans*-4-methoxystilbazole. It was expected that the Cp*Ru would coordinate to the more electron-rich, methoxy-substituted aromatic ring, hence enhancing its donor capacity. The new complex, $[Cp^*Ru(\eta^6$-*trans*-methoxystilbazole$)][CF_3SO_3]$, was characterized by spectroscopic methods and mass spectrometry. Particularly

indicative of the structure are the data from $^1$H NMR showing a shift of the aromatic protons of the methoxy substituted ring from $\delta$6.90 and 7.30 in the spectrum of the free ligand to $\delta$6.55 and 6.39 in the spectrum of the ruthenium complex, implying that the Cp*Ru fragment was in fact $\pi$-bound to this ring. The protons of the pyridine ring were also shifted from $\delta$8.55 and 7.40 in the free ligand to $\delta$8.93 and 8.11 for the complex. The two vinyl protons of the complex no longer had the appearance of a standard AB system and had collapsed into two singlets. The $^{13}$C NMR spectra also highlighted the coordination of the methoxy-substituted aromatic ring, the carbons being shifted to high field.

It is interesting to note that the ruthenium formed a $\pi$-bond with an aromatic ring rather than form a $\sigma$-bond with the nitrogen of the pyridine ring. This was perhaps surprising considering that few $\pi$-bound substituted pyridine complexes are known, the tendency being for the pyridine to form a $\sigma$-bond with the metal centre. The reaction of $[Cp^*Ru]^+$ with pyridine itself is complex and the product obtained depends on solvent polarity.[7] With isoquinoline, $^1$H NMR shows $\sigma$-coordination, whereas with quinoline, the data are consistent with $\pi$-coordination. Both 2,6- and 3,5-lutidine form $\pi$-complexes with Cp*Ru. In the case of 2,6-lutidine, this is not surprising as the nitrogen is highly sterically hindered, but it would be possible to form $\sigma$-bonded species with 3,5-lutidine, and yet the resulting complex is still $\pi$-coordinated. This again demonstrates the high propensity of the Cp*Ru fragment for forming $\pi$-bonded complexes.

*Complexes with improved acceptor groups*

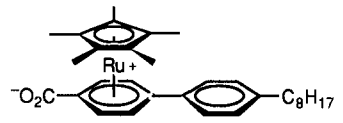
The mixed-metal complex shown below was synthesized as we had already established that $\beta$ increased on coordination of a stilbazole ligand to a $[MX(CO_2]$ (M = Rh, Ir) fragment.[8]




The complex was synthesized by mixing a 1:2 molar ratio of $[RhCl(CO)_2]_2$ and $[Cp^*Ru(\eta^6$-*trans*-4-methoxystilbazole)$]^+$ in dichloromethane. It was characterized by elemental analysis, IR spectroscopy and $^1$H and $^{13}$C NMR. The $^1$H peaks were broad at ambient temperature suggesting fluxionality. At low temperature, the $^1$H peaks were less broad and the NMR spectrum had separated into two complete sets of signals. This would seem to imply that two conformers were present, the interchange being slow on the NMR time-scale, although the identity of the two species is not clear.

An alternative method of improving the acceptor capacity of the pyridine group was to quaternize it. Both *trans*-4-methoxy-*N*-methylstilbazolium triflate and *trans*-4-methoxy-*N*-methylstilbazolium iodide were reacted with $[Cp^*Ru]^+$ as described before, but only the triflate system successfully $\pi$-bonded to the ruthenium *via* the methoxy-substituted ring. However, [Cp*Ru(*trans*-4-methoxy-*N*-methylstilbazolium)] diiodide was prepared successfully from the corresponding ditriflate compound by a simple anion metathesis.

The zwitterionic complex shown below ([Cp*Ru(4-octyloxy-4′-carboxylatebiphenyl)]) was also prepared as being neutral, it would be possible to evaluate $\beta$ by electric field-induced second harmonic generation (EFISH).




A similar complex, $[Cp^*Ru(\eta^6$-$PhCO_2)]$, was previously reported.[9]

Unfortunately, the complex formed was extremely insoluble and no NMR data or $\beta$ measurements could be obtained.

*Second harmonic generation*

All of the complexes mentioned above were tested for their ability to frequency double laser light of 1.06 $\mu$m using the Kurtz Powder technique.[10] Disappointingly, none showed any significant SHG (the limit of detection of the experiment was estimated to be 0.1 × urea) and so we concluded that although the chromophores synthesized would be expected to have a significant hyperpolarizability, this was not manifested in a measurable SHG response due to unoptimized packing in the solid state.

## EXPERIMENTAL

*Preparation of* trans-4-*methoxystilbazole*

This was synthesized by literature methods.[11] Yield 30.2 g; 78%. Found (calc.): C, 79.4 (79.6); H, 6.2 (6.2); N, 6.4 (6.6)%. UV/vis: $\lambda_{max}$ 325 nm ($\varepsilon$ 15,800 mol dm$^{-3}$ cm$^{-1}$), $CH_2Cl_2$.

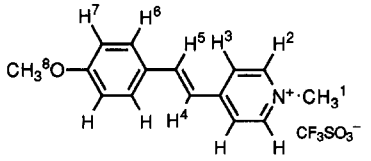
*Preparation of* 4-*octyloxybiphenyl-4′-carboxylic acid*

4-Octyloxy-4′-cyanobiphenyl (1 g, Merck) was dissolved in glacial acetic acid (16 $cm^3$) in a round-bottomed flask. A mixture of concentrated sulphuric acid (8 $cm^3$) and distilled water (8 $cm^3$) was added dropwise to the stirred solution. A condenser was fitted and the reaction mixture was heated under reflux for 48 h, after which it was allowed to cool and the white precipitate was collected by filtration. Yield 0.82 g; 77%. Found (calc.) C, 77.1 (77.3); H, 7.9 (8.0)%. Infrared: (KBr) $\nu_{CO}$ 1686 $cm^{-1}$.

*Preparation of* trans-4-*methoxy*-N-*methylstilbazolium triflate*

Methoxystilbazole (1.5 g, $7.1 \times 10^{-3}$ mol) was dissolved in outgassed dichloromethane (10 $cm^3$) in a Schlenk tube under argon. Methyltriflate (0.8 $cm^3$, $7.1 \times 10^{-3}$ mol) was added and the reaction was stirred for 1 h. The bright yellow precipitate that formed was collected by filtration and crystallized from dichloromethane. Yield 2.54 g; 95%. Found (calc.) C, 50.5 (51.2); H, 4.3 (4.3); N, 3.4 (3.7); S, 8.6 (8.5)%. Infrared: (KBr) $\nu_{SO}$ 1030 $cm^{-1}$. UV/vis: $\lambda_{max}$ 407 ($\varepsilon$ 16,700 mol $dm^{-3}$ $cm^{-1}$), $CH_2Cl_2$.

$^1$H NMR ($CD_2Cl_2$):

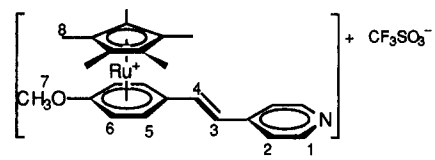



$H^1$: $\delta$3.87, (s, 3H); $H^2$: $\delta$8.50, (AA′XX′, 2H); $H^3$: $\delta$7.88, (AA′XX′, 2H), $H^4$, $H^5$: $\delta$7.65, $\delta$7.01, (AB, 2H); $H^6$: $\delta$7.62, (AA′XX′, 2H); $H^7$: $\delta$6.95, (AA′XX′, 2H); $H^8$: $\delta$4.29, (s, 3H).

*Preparation of* $\pi$-*bound ruthenium compounds*

*Preparation of* [Cp*Ru($\eta$-trans-4-*methoxystilbazole*)] *triflate*. The experiment was carried out under argon. $[Cp^*RuCl_2]_n$[12] (300 mg) and potassium carbonate, $K_2CO_3$ (0.550 g, excess) were placed in a Schlenk tube. Outgassed methanol (20 $cm^3$) was added and the mixture was stirred under reflux for 20 min until the solution turned purple. After removing the solvent under vacuum, [Cp*Ru$(OCH_3)]_2$ was extracted into outgassed THF (20 $cm^3$, 10 $cm^3$), and the solution was filtered to remove the unreacted $K_2CO_3$ residue. Triflic acid (90 $\mu$l, 1 mol. equiv.) was then added to the purple solution which was stirred for 10 min to give the orange/brown '$[Cp^*Ru]^+[CF_3SO_3]^-$' species in solution. *Trans*-4-Methoxystilbazole (0.206 g, 1 mol. equiv.) was dissolved in outgassed THF (5 $cm^3$) in a Fischer–Porter tube, into which the orange/brown '$[Cp^*Ru]^+CF_3SO_3^-$' solution was transferred by cannula. The mixture was heated (85°C) and stirred for 24 h. On cooling, the solution was transferred by a cannula into a Schlenk tube (any red oil remaining in the Fischer–Porter tube was dissolved in more THF and also transferred to the Schlenk tube). The solution was evaporated to dryness *in vacuo* and the remaining solid was washed with diethyl ether (20 $cm^3$) and pentane (20 $cm^3$). The solid was then washed with dichloromethane (3 $cm^3$), giving an orange powder, which was crystallized from acetone. (The product was soluble to an extent in dichloromethane, therefore the washings were retained and concentrated to give an orange solid which was treated as above.) Yield 0.15 g; 26%. Infrared: $\nu_{SO}$ 1026 $cm^{-1}$. UV/vis: $\lambda_{max}$ 389 nm ($\varepsilon$ 17400 mol $dm^{-3}$ $cm^{-1}$), $CH_2Cl_2$. Mass spectrometry: molecular ion $M/z$ 597; [Cp*Ru($\eta$-*trans*-4-methoxystilbazole)] fragment $M/z$ 448.

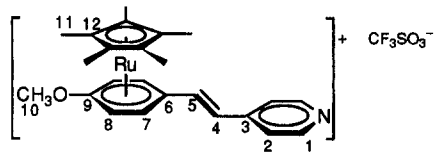
$^1$H NMR ($CD_3COCD_3$):




It can be seen that the 'Cp*Ru' fragment is $\pi$-bound to the methoxy-substituted ring as $H^5$ and $H^6$ are significantly shifted as comparable with the spectrum of the free *trans*-4-methoxystilbazole ligand ($\delta$7.35 and $\delta$6.90, respectively).

AA′XX′: $H^1$: $\delta$8.93, (2H), $H^2$: $\delta$8.11, (2H)$-J = 7$ Hz; AA′XX′: $H^3$, $H^4$: $\delta$7.70, (d, 2H); $H^5$: $\delta$6.55, (d, 2H)$-J = 7$ Hz; $H^6$: $\delta$6.39, (d, 2H); $H^7$: $\delta$4.06, (s, 3H); $H^8$: $\delta$2.09, (s, 15H).

$^{13}$C NMR ($CH_3COCD_3$):



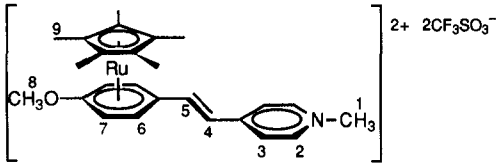

$C^1$: $\delta$147.2; $C^2$: $\delta$130.8; $C^3$: $\delta$133.4; $C^4$, $C^5$: $\delta$122.8, $\delta$114.8; $C^6$: $\delta$94.3; $C^7$: $\delta$84.99; $C^8$: $\delta$76.5; $C^9$: $\delta$147.8; $C^{10}$: $\delta$57.0; $C^{11}$: $\delta$9.8; $C^{12}$: $\delta$96.5.

*Preparation of* [Cp*Ru($\eta$-4-*octyloxybiphenyl-4′-carboxylate*)]. The same method was used as for [Cp*Ru($\eta$-*trans*-4-methoxystilbazole)] triflate, up

to the point of generating the Cp*Ru fragment. This solution was then transferred by cannula into a Schlenk tube containing an outgassed solution of 4-octyloxybiphenyl-4′-carboxylate. A white/grey precipitate formed which was collected by filtration and washed with diethyl ether (20 $cm^3$), pentane (20 $cm^3$), acetone (20 $cm^3$) and acetonitrile (20 $cm^3$). Yield 0.42 g; 26%. Found (calc.) C, 66.9 (66.3); H, 7.1 (7.2)%. Infrared: (KBr) $\nu_{CO}$ 1604 $cm^{-1}$, 1399 $cm^{-1}$. Mass spectrometry: molecular ion $M/z$ 563.

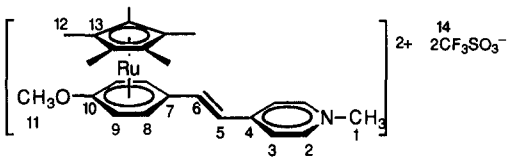
*Preparation of* [Cp*Ru(η-trans-4-*methoxy*-N-*methylstilbazolium*)] *ditriflate*. The same method was used as for [Cp*Ru(η-*trans*-4-methoxystilbazole)], only using *trans*-4-methoxy-*N*-methylstilbazolium triflate in the final step. Yield 0.510 g; 22%. Found (calc.) C, 42.1 (42.6); H, 4.2 (4.1); N, 1.8 (1.8); S, 8.4 (8.4)%. Infrared: (KBr) $\nu_{SO}$ 1032 $cm^{-1}$. UV/vis: $\lambda_{max}$ 408 nm (ε 23,400 mol $dm^{-3}$ $cm^{-1}$), $CH_2Cl_2$.

$^1$H NMR ($d^6$-acetone):




$H^1$: δ2.95, (s, 3H); $H^2$: δ8.97, (AA′XX′, 2H); $H^3$: δ8.39, (ZZ′XX′, 2H) − $J$ = 7 Hz; $H^4$, $H^5$: δ7.50, δ7.62, (AB, 2H − $J_{AB}$ = 17 Hz); $H^6$: δ6.46, (AA′XX′, 2H); $H^7$: δ6.26, (AA′XX′, 2H) − $J$ = 7 Hz; $H^8$: δ4.55, (s, 3H); $H^9$: δ1.89, (s, 15H).

$^{13}$C NMR($CD_3COCD_3$):

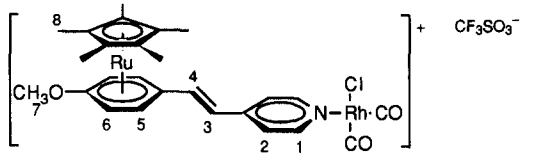



$C^1$: δ48.17; $C^4$: δ134.10; $C^7$: δ93.61; $C^8$: δ85.91; $C^9$: δ77.07; $C^{10}$: δ152.56; $C^{11}$: δ57.46; $C^{12}$: δ10.17; $C^{13}$: δ97.20; $C^{14}$: δ122.09, ($q$, $J_{CF}$ 320 Hz); $C^2$, $C^3$, $C^5$, $C^6$: δ125.44, δ128.96, δ136.23, δ146.43.

*Preparation of* [Cp*Ru(η-trans-4-*methoxy*-N-*methylstilbazolium*)] *diiodide*. [Cp*Ru(η-*trans*-4-methoxy-*N*-methylstilbazolium)] bis(triflate) (70 mg, 9.2. × $10^{-5}$ mol) and tetrabutylammonium iodide (326 mg, 2 mol. equiv.) were placed in a Schlenk tube under argon. Outgassed acetone (10 $cm^3$) was added and the reaction mixture was stirred overnight. The yellow precipitate that formed was collected by filtration. Yield 60 mg; 91%. Found (calc.) C, 41.5 (41.9); H, 4.4 (4.4); N, 1.9 (2.0); S, 35.5 (35.4)%. (UV/vis: $\lambda_{max}$ 316 nm (ε 23100 mol $dm^{-3}$ $cm^{-1}$), $CH_2Cl_2$. $^1$H NMR ($CD_3COCD_3$): the spectrum was assigned as for [Cp*Ru(η-*trans*-4-methoxy-*N*-methylstilbazolium)] bis(triflate).

*Preparation of* [Cp*Ru(η-trans-4-*methoxystilbazole*-cis-$Rh(CO)_2(Cl)$] *triflate*. [Cp*Ru(η-*trans*-4-methoxystilbazole)] triflate (110 mg, 1.84 × $10^{-4}$ mol) and $[Rh(CO)_2Cl]_2$ (36 mg, 0.5 mol. equiv.) were dissolved in outgassed dichloromethane (10 $cm^3$) in a Schlenk tube and stirred under argon for 30 min. Hexane (10 $cm^3$) was added and the dichloromethane was removed under vacuum. The yellow precipitate obtained was collected by filtration, washed with pentane (2 × 10 $cm^3$) and diethyl ether (10 $cm^3$). Yield 88 mg; 63%. Found (calc.), C, 40.4 (41.0); H, 4.1 (3.6); N, 1.6 (1.8); S, 4.4 (4.1)%. Infrared: (dichloromethane) $\nu_{CO}$ 2087, 2014 $cm^{-1}$; (KBr) $\nu_{CO}$ 2078, 2013, 2000 $cm^{-1}$. UV/vis: $\lambda_{max}$ 340 nm (ε 26,900 mol $dm^{-3}$ $cm^{-1}$), $CH_2Cl_2$.

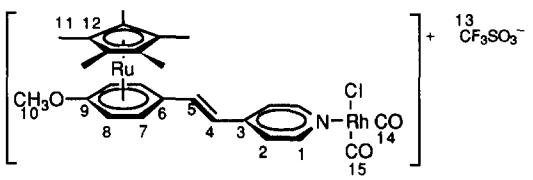
$^1$H NMR ($CD_3COCD_3$):




At ambient temperature: all aromatic signals were broad. Total unsaturated integration was equivalent to 10 protons. $H^1$: δ8.77; $H^2$: δ7.88; $H^3$, $H^4$: δ7.55; $H^5$: δ6.43; $H^6$: δ6.36; $H^7$: δ3.93, (s, 3H); $H^8$: δ1.96, (s, 15H).

At low temperature (183K): signals were less broad. Total aromatic integration was equivalent to 10 protons. The two protons numbered 1 were no longer in an equivalent environment. The same was true for the protons numbered 2. $H^1$: δ9.09, (m), δ8.95, (m); $H^2$: δ8.71, (m), δ8.44, (m); $H^3$, $H^4$: δ7.75, (m); $H^5$: δ6.40, (m); $H^6$: δ6.25, (s, br.); $H^7$: δ3.85, (m); $H^8$: δ1.87, (s).

$^{13}$C NMR ($CD_3COCD_3$):




At ambient temperature: $C^3$: δ134.0; $C^6$: δ94.7; $C^7$: δ85.7; $C^8$: δ77.0; $C^9$: δ148.3; $C^{10}$: δ57.5; $C^{11}$: δ10.3; $C^{12}$: δ97.1; $C^1$, $C^2$, $C^4$, $C^5$: δ132.6, δ130.5, δ124.1, δ115.9.

At low temperature (183K): $C^3$: δ146.4; $C^6$: δ92.9; $C^7$: δ83.8; $C^8$: δ75.2; $C^9$: δ152.3; $C^{10}$: δ4.5; $C^{11}$: δ9.0; $C^{12}$: δ95.4; $C^1$, $C^2$, $C^4$, $C^5$: δ141.7, δ132.3,

$\delta$130.5, $\delta$128.9, $\delta$127.8, $\delta$123.7, $\delta$123.0, $\delta$122.4. The peaks assigned to carbons 1, 2, 4, 5, 6, 7, 8, 10 and 12 in the spectrum taken at ambient temperature all appeared as two lines in the low temperature spectrum.

*Acknowledgements*—We thank SERC (AT) for support, Johnson Matthey for generous loans of rhodium salts and NATO for the provision of a collaborative grant to DWB and BC.

## REFERENCES

1. S. R. Marder, in *Inorganic Materials* (Edited by D. W. Bruce and D. O'Hare). Wiley, Chichester (1992).
2. (a) C. Bertram, D. W. Bruce, D. A. Dunmur, S. E. Hunt, P. M. Maitlis and M. McCann, *J. Chem. Soc., Chem. Commun.* 1991, 69; (b) D. W. Bruce, D. A. Dunmur. M. R. Manterfield, P. M. Maitlis and R. Orr, *J. Mater. Chem.* 1991, **1**, 255.
3. L. T. Cheng, W. Tam, G. R. Meredith and S. R. Marder, *Mol. Cryst. Liq. Cryst.* 1990, **189**, 137.
4. S. R. Marder, J. W. Perry, W. P. Schaefer, B. G. Tiemann, P. C. Groves and K. J. Perry, *Proc. Spie. Int. Opt. Soc.* 1989, **1147**, 108.
5. M. Kimura, H. Abdel-Halim, D. W. Robinson and D. O. Cowan, *J. Organomet. Chem.* 1991, **403**, 365.
6. S. G. Davies, A. J. Smallridge, R. Colbrook, T. Richardson and G. G. Roberts, *J. Organomet. Chem.* 1991, **401**, 181.
7. (a) B. Chaudret, F. Jalon, M. Perez-Manrique, F. Lahoz, F. J. Plou and R. Sanchez-Delgado, *New J. Chem.* 1990, **14**, 331; (b) X.-D. He, B. Chaudret, F. Dahan and Y. S. Huang, *Organometallics* 1991, **10**, 970; (c) D. Rondon, B. Chaudret, X.-D. He and D. Labroue, *J. Am. Chem. Soc.* 1991, **113**, 5671; (d) Y. S. Huang, S. Sabo-Etienne, X.-D. He, B. Chaudret, K. Boubekeur and P. Batail, *Organometallics* 1992, **11**, 3031; (e) F. Urganos, M. A. Halcrow, J. Fernandez-Baeza, F. Dahan, D. Labroue and B. Chaudret, *J. Am. Chem. Soc.* 1993, **115**, 3484.
8. D. W. Bruce and A. Thornton, *Mol. Cryst. Liq. Cryst.* 1993, **231**, 253.
9. B. Chaudret, X.-D. He and Y. Huang, *J. Chem. Soc., Chem. Commun.* 1989, 1844.
10. S. K Kurtz and J. T. Perry, *J. Appl. Phys.* 1968, **39**, 3798.
11. D. W. Bruce, D. A. Dunmur, E. Lalinde, P. M. Maitlis, and P. Styring, *Liq. Cryst.* 1988, **3**, 385.
12. U. Koelle and J. Kossakowski, *Inorg. Synth.* 1992, **29**, 225.