Pergamon

0277-5387(94)00450-1

Polyhedron Vol. 14, No. 13-14, pp. 1915-1922, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277-5387/95 $9.50+0.00

THE SYNTHESIS AND CHARACTERIZATION OF POTENTIALLY MESOMORPHIC CARBONYL COMPLEXES OF TUNGSTEN(0) WITH SUBSTITUTED PYRIDINES

DUNCAN W. BRUCE*† AND JONATHAN P. ROURKE‡

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

(*Received* 14 *October* 1994; *accepted* 24 *October* 1994)

Abstract—Some new tungsten carbonyl complexes have been synthesized with stilbazole type ligands. Their potential as liquid crystals is discussed.

There is currently much interest in the synthesis of metal-containing liquid crystals due to the perceived advantages of combining the properties of liquid crystal systems with those of transition metals. The area has been well reviewed recently.[1] On reading such reviews, it is immediately apparent that the vast majority of mesomorphic complexes are derived from metals in the d^8–d^{10} electron configurations, usually with planar or linear geometries. While these complexes have proved both interesting and rewarding to study, many metals are excluded in concentrating on these systems. Planar and linear complexes are of course preferred for the synthesis of rod-like (calamitic) materials, as the shapes of the resulting complexes closely resemble the anisotropic rods formed by organic systems and one can quickly imagine that the inclusion of an octahedral metal centre would act severely to modulate this anisotropy.[2]

However, we reasoned that if a sufficiently large liquid crystalline ligand were employed, then the perturbation of the anisotropy due to the metal fragment could be minimized. We have recently demonstrated the viability of this approach with the synthesis of mesomorphic manganese(I)[3] and rhenium(I)[4] carbonyls. As we have previously worked extensively with substituted pyridine ligands,[5,6] we felt that this might be an appropriate starting point and we chose to examine their simple coordination chemistry with the [W(CO)$_5$] moiety.

RESULTS AND DISCUSSION

The synthesis of substituted tungsten carbonyl compounds is relatively straightforward and the two routes outlined in Fig. 1 were first reported in 1963.[7] This original paper dealt with the case when L = pyridine.

We used these two routes to synthesize successfully a number of compounds where L was a substituted pyridine. The geometry of both the monosubstituted pentacarbonyl (**1**) and the disubstituted tetracarbonyl (**2**) were determined by IR spectroscopy.[7] The monosubstituted pentacarbonyl (**1**) exists in an octahedral geometry (C_{4v}), as does the disubstituted tetracarbonyl (**2**); here, the geometry is exclusively *cis* (C_{2v}).

The ligands used are illustrated in Fig. 2 and all are stilbazoles. In the 'free' state, the ligand **A** showed a narrow-range smectic B phase above a wider range crystal smectic E phase.[8] Ligand **B** was marginally mesomorphic, showing only a crystal phase between 236 and 238°C. Ligand **C** showed a varied polymorphism, including a smectic A phase between 115 and 176°C.[9]

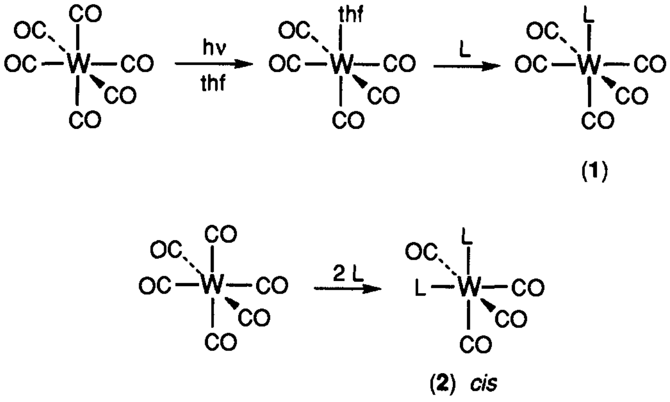
Both types of complex were successfully synthesized for the three different ligands illustrated above, and were fully characterized by NMR and

---

* Author to whom correspondence should be addressed.

† D.W.B. is the Sir Edward Frankland Fellow of the Royal Society of Chemistry, 1994/95.

‡ Current address: Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.



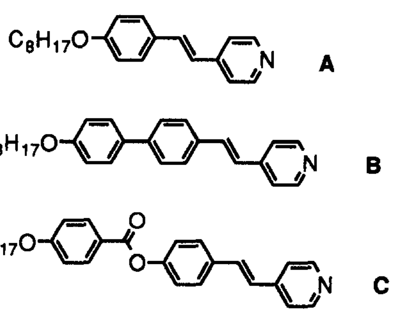
(1)

(2) *cis*

Fig. 1. Preparation of the new complexes.

IR spectroscopy, and elemental analysis. The complexes will be denoted **1A** etc.

Both types of tungsten complex were very intensely coloured: the monosubstituted compounds **1** were yellow and the disubstituted complexes **2** red. Compounds **1** had a tendency to disproportionate and in solution turned orange upon heating as the disubstituted compound **2** and $W(CO)_6$ were formed. The disubstituted compound **2** had a tendency to react in solution in what appeared to be an oxidative manner, as it was possible for **2C** to watch the progress of the 'reaction' down an NMR tube with time. Thus, the red disubstituted complex would turn yellow and show the IR spectrum of a monoligand pentacarbonyl species (**1**). The NMR showed the appearance of a new doublet centred at δ 8.65, which appeared to be due to half of the AA′XX′ pattern of a new set of α-pyridyl protons, with the other half appearing centred at δ 7.1. The other new signal to appear was half of an AB system centred at δ 6.45, with $J = 13$ Hz, strongly suggestive of a *cis* arrangement about the stilbazole vinyl link. Isomerization of stilbazoles is well known[10]. Eventually, the NMR spectrum shows the loss of all *trans*-stilbazole. Isolation and characterization of the yellow compound gave a result in which the carbon percentage was around 8% lower than that expected for a complex of the type **2**, even though the hydrogen and nitrogen percentages were in agreement with this formulation. Despite all of the above information, this yellow product has resisted full characterization.



A

B

C

Fig. 2. Ligands used for complexation.

As solids, in air at room temperature, both complexes **1** and **2** appeared to be stable for at least a month. Upon heating, however, the monosubstituted compound **1** once again turned red and the disubstituted compound **2** could be isolated. The stability of these complexes, as a function of the ligand, seems to increase in the order: **C** < **A** < **B**. Thus, a solution of the disubstituted complex of **C** turned yellow in 5 min, whereas a solution of the related complex with ligand **B** remained undecomposed (by IR) after 2 h.

Thermal properties

The tendency of the monosubstituted complexes **1** to undergo some sort of disproportionation made identification of any mesomorphism impossible, and all three monosubstituted complexes turned red upon heating prior to melting. The approximate temperatures of decomposition are 98°C for **1A**, 84°C for **1B** and 132°C for **1C**.

The disubstituted complexes **2**, however, were more interesting. Complex **2A** melted cleanly at 112°C, and showed no unusual behaviour on cooling, even to −30°C, where it appeared to form a glass rather than crystallize. Likewise, complex **2C** melted cleanly at 168°C, showed no unusual behaviour on cooling to 30°C, and again it appeared to form a glass. Complex **2B** appeared to undergo a crystal–crystal transition at around 125°C (the colour changed to an even darker red–purple) and appeared to go into a phase with a Schlieren texture at 195°C, before decomposing at

207°C. These transitions were also observed in the DSC:

124.7°C	12.1 kJ mol^{-1} (Cry–Cry′)
182.6°C	3.5 kJ mol^{-1} (Cry′–Cry″)
196.8°C	25.8 kJ mol^{-1} (Cry″–M)
220°C	Decomp.

Cry, Cry′ and Cry″ are crystal phases, while M represents an unidentified liquid crystal mesophase.

The Schlieren type phase has not been assigned as the intense colour of these systems, coupled with their poor stability, has rendered identification all but impossible.

The results obtained for the monosubstituted complexes were rather disappointing and we believe that the instability of these complexes with respect to disproportionation was the reason that mesomorphic materials were not obtained. Clearly, more stable materials of this type need to be targeted. Presumably, ligands with a smaller *cis* influence would be the best prospect. The results obtained from the disubstituted complex **2B** were much more interesting and the observation of a fluid, Schlieren texture suggests that the phase was nematic, SmC or possibly SmI. Obtaining more stable derivatives of this type of complex is probably more straightforward and these studies are already underway.

EXPERIMENTAL

Elemental analyses were performed by the Sheffield Microanalytical service. NMR spectra were performed on a Bruker ACL-250 in $CDCl_3$, and are referenced to external tetramethylsilane. Proton and carbon assignments were made via the JMOD and COSY pulse sequences. DSC measurements were performed on a Perkin–Elmer DSC7 operating TAS7 software: the heating rate used was 10 K min^{-1}. Optical characterization was performed using a Zeiss Lab-Pol polarizing microscope with a Linkam temperature controller.

Tetrahydrofuran (thf) was freshly distilled prior to use; all other chemicals were used as supplied.

Ligand **A** was prepared by the literature method,[5] while **C** was obtained using a small variation on the method described by Kumar *et al.*[11]

Synthesis of ligand B

A mixture of 4′-octyloxy-4-bromobiphenyl (29.9 g, 8.28×10^{-2} mol), 4-vinylpyridine (9.58 g, 9.11×10^{-2} mol), triethylamine (8.36 g, 8.28×10^{-2} mol), palladium acetate (0.185 g, 8.28×10^{-4} mol) and tri(*o*-tolyl)phosphine (0.501 g, 1.66×10^{-3} mol) was dissolved in acetonitrile (100 cm^3) in a Fischer–Porter tube fitted with Teflon seals. After filling with argon, the tube was sealed and heated at 80–100°C for 6 days. The mixture was allowed to cool and everything dissolved in dichloromethane (800 cm^3). The solution was washed (water, 700 cm^3) and dried (K_2CO_3). The solvent was removed and the resultant mixture stirred with pentane (500 cm^3, 30 min). The off-white product was collected by filtration and washed with a small volume of dichloromethane. Yield: 26.9 g (84%, 6.96×10^{-2} mol). Found: C, 83.8; H, 8.1; N, 3.6. $C_{27}H_{31}NO$ requires: C, 84.1; H, 8.1; N, 3.6%. NMR data: see Table 1.

Synthesis of [W(CO)$_5$(B)]

Tungsten hexacarbonyl (1.02 g, 2.86×10^{-3} mol) was dissolved in thf (30 cm^3) and photolysed (medium pressure mercury source) under an N_2 purge (16 h). The resultant yellow solution had an IR spectrum which indicated almost complete transformation to [W(CO)$_5$(thf)] [ν(CO) at 2074 (w), 1930 (vs) and 1890 (s) cm^{-1}]. Ligand **B** (1.10 g, 2.86×10^{-3} mol) was added to thf (15 cm^3) and the mixture was stirred (5 min), during which time the colour darkened to orange. The solvent was removed under reduced pressure and then the flask evacuated at 40°C until there was no trace of W(CO)$_6$ by IR. Chromatography of the product on silica with a pentane–dichloromethane mixture (1 : 1) effected the separation of the yellow [W(CO)$_5$(**B**)] from any red *cis*-[W(CO)$_4$(**B**)$_2$]. Both compounds could be isolated in analytical purity, though very little of the disubstituted product was actually collected. Yield: 1.17 g (55%). The analogous complexes **1A** and **1C** were synthesized in the same way. Microanalytical data are collected in Table 2. IR (CH_2Cl_2): **1A**, 2071 (w), 1973 (sh), 1928 (vs) and 1891 (s) cm^{-1}; **1B**, 2070 (w), 1972 (sh), 1928 (vs) and 1897 (s) cm^{-1}; **1C**, 2071 (w), 1972 (sh), 1928 (vs) and 1898 (s) cm^{-1}. ^{1}H NMR: see Tables 3–5.

Synthesis of cis-[W(CO)$_4$(B)$_2$]

Ligand **B** (1.21 g, 3.14×10^{-3} mol) and tungsten hexacarbonyl (0.61 g, 1.57×10^{-3} mol) were heated together under argon in the absence of solvent. At 120°C, a yellow tint was observed and at 180°C, a dark red colour was observed. The mixture was maintained at the higher temperature for 30 min, when the conversion to the red product appeared total. Unreacted white W(CO)$_6$ was sublimed out of the reaction vessel, and the resulting mixture separated using flash chromatography on silica with CH_2Cl_2 as mobile phase. This yielded the pure product. Yield: 1.19 g (69%). The analogous complexes **2A** and **2C** were synthesized in the same way.

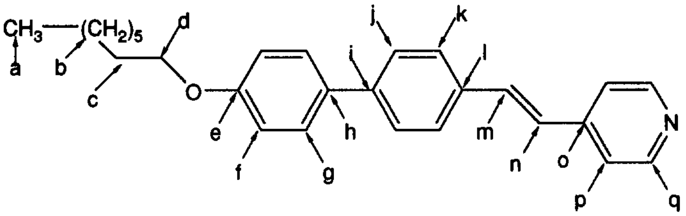


Table 1. NMR data for ligand **B**

	δ	No. of protons	Multiplicity	Identity
^{1}H	0.89	3H	t	H_a
	1.30	10H	m	H_b
	1.82	2H	m	H_c
	4.02	2H	t	H_d
	6.97	2H	(AX)′	H_f
	7.03	1H	d, ^3J(HH) = 17 Hz	H_n
	7.33	1H	d, ^3J(HH) = 17 Hz	H_m
	7.37	2H	(AX)′	H_p
	7.55	2H	(AX)′	H_g
	7.58	4H	s	H_{j+k}
	8.56	2H	(AX)′	H_q
	δ	Carbon	δ	Carbon
^{13}C	14.1	C_a	22.7	C_b
	26.0	C_b	29.3	C_b
	29.4	C_c	31.9	C_b
	68.1	C_d	114.9	C_f
	120.8	C_p	125.5	C_n
	126.9	$C_{j/k}$	127.5	$C_{j/k}$
	128.0	C_g	132.6	C_h
	132.9	C_m	134.4	C_l
	141.2	C_i	144.8	C_o
	150.2	C_q	159.1	C_e

Table 2.

		Microanalysis (calc.)		
Compound	Chain	%C	%H	%N
1A	8	50.9 (50.9)	4.7 (4.7)	2.0 (2.1)
1B	8	54.3 (54.2)	4.5 (4.4)	1.7 (1.9)
1C	8	52.3 (52.6)	4.2 (4.1)	1.8 (1.9)
2A	8	61.6 (61.9)	6.5 (6.4)	2.8 (2.9)
2B	8	65.1 (65.3)	5.9 (5.9)	2.3 (2.6)
2C	8	62.3 (62.4)	5.4 (5.4)	2.3 (2.4)

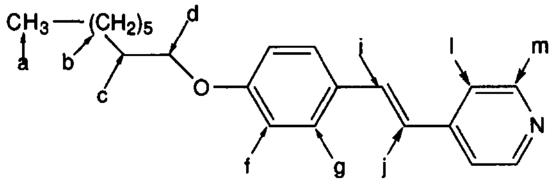


Table 3. ^{1}H NMR data for compound **1A**

δ	No. of protons	Multiplicity	Identity
0.81	3H	t	H_a
1.30	10H	m	H_b
1.78	2H	m	H_c
3.95	2H	t	H_d
6.73	1H	d, ^3J(HH) = 16 Hz	$H_{i,j}$
6.82	2H	(AX)′	H_f
7.12	2H	(AX)′	H_l
7.25	1H	d, ^3J(HH) = 16 Hz	$H_{i,j}$
7.39	2H	(AX)′	H_g
8.52	2H	(AX)′	H_m

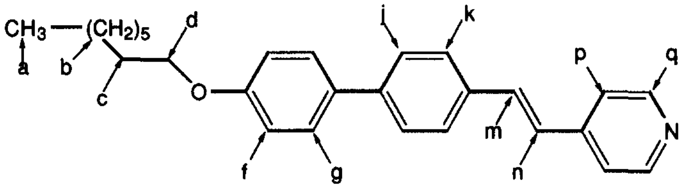


Table 4. ^{1}H NMR data for compound **1B**

δ	No. of protons	Multiplicity	Identity
0.81	3H	t	H_a
1.30	10H	m	H_b
1.78	2H	m	H_c
3.94	2H	t	H_d
6.91	2H	(AX)′	H_f
6.93	1H	d, ^3J(HH) = 16 Hz	$H_{m,n}$
7.26	2H	(AX)′	H_p
7.33	1H	d, ^3J(HH) = 16 Hz	$H_{m,n}$
7.50	2H	(AX)′	H_g
7.52	4H	s	H_{j+k}
8.65	2H	(AX)′	H_q

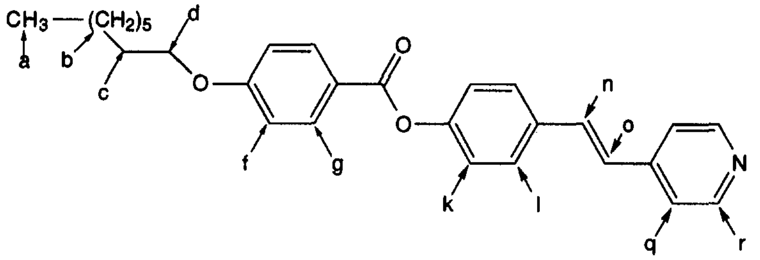


Table 5. ^{1}H NMR data for compound **1C**

δ	No. of protons	Multiplicity	Identity
0.81	3H	t	H_a
1.30	10H	m	H_b
1.78	2H	m	H_c
4.00	2H	t	H_d
6.88	1H	d, ^3J(HH) = 16 Hz	$H_{n,o}$
6.91	2H	(AX)′	H_k
7.24	2H	(AX)′	$H_{f,q}$
7.26	2H	(AX)′	$H_{f,q}$
7.30	1H	d, ^3J(HH) = 16 Hz	$H_{n,o}$
7.55	2H	(AX)′	H_l
8.06	2H	(AX)′	H_g
8.68	2H	(AX)′	H_r

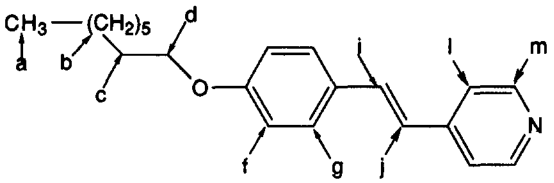


Table 6. ^{1}H NMR data for compound **2A**

δ	No. of protons	Multiplicity	Identity
0.81	3H	t	H_a
1.30	10H	m	H_b
1.78	2H	m	H_c
3.95	2H	t	H_d
6.71	1H	d, ^3J(HH) = 16 Hz	$H_{i,j}$
6.82	2H	(AX)′	H_f
7.19	2H	(AX)′	H_l
7.23	1H	d, ^3J(HH) = 16 Hz	$H_{i,j}$
7.38	2H	(AX)′	H_g
8.47	2H	(AX)′	H_m

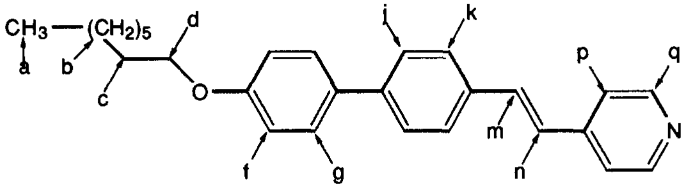


Table 7. ^1H NMR data for compound **2B**

δ	No. of protons	Multiplicity	Identity
0.81	3H	t	H_a
1.30	10H	m	H_b
1.78	2H	m	H_c
3.95	2H	t	H_d
6.90	1H	d, $^3J(HH) = 16$ Hz	$H_{m,n}$
6.91	2H	(AX)′	H_f
7.19	2H	(AX)′	H_p
7.29	1H	d, $^3J(HH) = 16$ Hz	$H_{m,n}$
7.48	2H	(AX)′	H_g
7.52	4H	s	H_{j+k}
8.59	2H	(AX)′	H_q

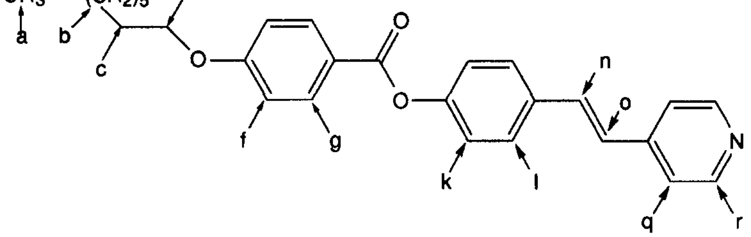


Table 8. ^1H NMR data for compound **2C**

δ	No. of protons	Multiplicity	Identity
0.81	3H	t	H_a
1.30	10H	m	H_b
1.78	2H	m	H_c
4.00	2H	t	H_d
6.87	1H	d, $^3J(HH) = 16$ Hz	$H_{n,o}$
6.91	2H	(AX)′	H_k
7.24	2H	(AX)′	$H_{f,q}$
7.25	2H	(AX)′	$H_{f,q}$
7.27	1H	d, $^3J(HH) = 16$ Hz	$H_{n,o}$
7.55	2H	(AX)′	H_l
8.06	2H	(AX)′	H_g
8.62	2H	(AX)′	H_r

Microanalytical data are collected in Table 2. IR (CH_2Cl_2): **2A**, 2001 (w), 1873 (vs), 1868 (vs) and 1823 (s) cm^{-1}; **2B**, 2004 (w), 1875 (vs), 1867 (vs) and 1826 (s) cm^{-1}; **2C**, 2003 (w), 1876 (vs), 1866 (vs) and 1825 (s) cm^{-1}. ^1H NMR: see Tables 6–8.

Acknowledgements—We acknowledge the SERC 21st Century Materials Initiative and Molecular Electronics Committee and the University of Sheffield for support to J. P. R.

REFERENCES

1. D. W. Bruce, in *Inorganic Materials* (Edited by D. W. Bruce and D. O'Hare). Wiley, Chichester (1992); A.-M. Giroud-Godquin and P. M. Maitlis, *Angew. Chem., Int. Edn. Engl.* 1991, **30**, 375; P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.* 1992, **117**, 215; S. A. Hudson and P. M. Maitlis, *Chem. Rev.* 1993, **93**, 861.
2. D. W. Bruce, *Adv. Mater.* 1944, **6**, 1017.
3. D. W. Bruce and X.-H. Liu, *J. Chem. Soc., Chem. Commun.* 1994, 729.
4. D. W. Bruce and X.-H. Liu, *Liq. Cryst.* 1995, **18**, 165.
5. D. W. Bruce, D. A. Dunmur, M. A. Esteruelas, S. E. Hunt, R. Le Lagadec, P. M. Maitlis, J. R. Marsden, E. Sola and J. M. Stacey, *J. Mater. Chem.* 1991, **1**, 251; C. Bertram, D. W. Bruce, D. A. Dunmur, S. E. Hunt, P. M. Maitlis and M. McCann, *J. Chem. Soc., Chem. Commun.* 1991, 69; H. Adams, N. A. Bailey, D. W. Bruce, S. A. Hudson and J. R. Marsden, *Liq. Cryst.* 1994, **16**, 643.
6. H. Adams, N. A. Bailey, D. W. Bruce, S. C. Davis, D. A. Dunmur, P. D. Hempstead, S. A. Hudson and S. J. Thorpe, *J. Mater. Chem.* 1992, **2**, 395; D. W. Bruce, D. A. Dunmur, S. A. Hudson, E. Lalinde, P. M. Maitlis, M. P. McDonald, R. Orr, P. Styring, A. S. Cherodian, R. M. Richardson, J. L. Feijoo and G. Ungar, *Molec. Cryst. Liq. Cryst.* 1991, **206**, 79.
7. C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.* 1963, **2**, 533.
8. D. W. Bruce, D. A. Dunmur, E. Lalinde, P. M. Maitlis and P. Styring, *Liq. Cryst.* 1988, **3**, 385.
9. T. Katfo and J. M. J. Fréchet, *Macromolecules* 1990, **20**, 360.
10. G. L. Gaines, *Angew. Chem., Int. Edn Engl.* 1987, **26**, 341 and references therein.
11. U. Kumar, T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.* 1992, **114**, 6630.