

Thio-Analogues of 2-(1*H*-Heteroaryliden)-1*H*-indene-1,3(2*H*)-diones, Synthesis and Formation of Metal Complexes

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2-(1*H*-Heteroaryliden)-1*H*-indene-1,3(2*H*)-diones were converted into anils and dianils and then into monothio- and dithio-derivatives by treatment with hydrogen sulphide. The 2-pyridinyl monothioderivate was converted into S-alkyl ethers. In contrast with the dione **1** the thio-derivatives readily formed isolable complexes with transition metals. Spectroscopic and magnetic data are reported.

(Keywords: Electronic spectra; Metal complexes; Thiopyrophthalone)

Thio-Analoge von 2-(1H-Heteroarylidene)-1H-inden-1,3(2H)-dionen. Synthese und Bildung von Metallkomplexen

2-(1*H*-Heteroaryliden)-1*H*-inden-1,3(2*H*)-dione wurden in Anile und Dianile und durch anschließende Behandlung mit Schwefelwasserstoff in die entsprechenden Mono- und Di-thio-derivate umgewandelt. Aus den 2-Pyridinyl-monothio-derivaten wurden S-Alkyl-ether erhalten. Im Gegensatz zum Dion **1** bildeten die Thioderivate glatt isolierbare Komplexe mit Übergangsmetallen. Spektroskopische und magnetische Daten werden mitgeteilt.

Introduction

In continuation of our previous studies on the thio-analogues of 1*H*-inden-1,3(2*H*)-diones¹⁻³ we describe the conversion of the diones **1-3** (pyrophthalone, quinophthalone and isoquinophthalone) into the corresponding monothio- and dithio-derivatives **4-9** in high yields and the formation of S-alkyl ethers **19-21** and transition metal complexes **22-28**.

Results

Treatment of the diones **1** and **2** with aluminium chloride followed by aniline, as previously described^{4,5}, gave the anils **10** and **11** respectively. A similar reaction with the isoquinolinylidene dione **3** gave a mixture of the anil **12** and the imino-enamine **13** formed by reaction with two equivalents of aniline and, for convenience, referred to as the dianil. Reaction of aniline with the diones **1** and **2** catalysed by titanium chloride conveniently afforded the dianils **14** and **15** respectively. The monothio- and dithio-derivatives **4-9** were prepared by treating the corresponding anils and dianils with hydrogen sulphide.

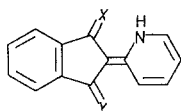
Table 1. *N.m.r. spectra of anils and dianils 10-18*

No.	δ (CDCl ₃)
10	13.50 (NH), 8.75 (sextet, 3'-H, J 8.3 Hz), 8.45 (m, 6'-H), 7.7-6.9 (10H, m) and 6.46 (m, 4-H)
11	15.00 (NH), 8.90 (d, 3'-H, J 8.9 Hz), 8.00 (d, 4'-H), 7.85-6.90 (12H, m) and 6.50 (m, 4-H)
12	13.00 (NH), 9.00 (2H, s, 1'-H, 4'-H), 8.00-6.85 (12H, m) and 6.44 (m, 4-H)
13	12.45 (NH), 9.35 (s, 4'-H), 9.17 (s, 1'-H) and 8.00-6.40 (18H, m)
14	13.00 (NH), 9.13 (m, 3'-H), 8.76 (m, 6'-H) and 7.90-6.40 (16H, m)
15	14.00 (NH), 9.20 (d, 3'-H), 8.15 (d, 4'-H) and 7.90-6.40 (18H, m)
16	8.58 (m, 6'-H), 7.70-6.80 (11H, m), 5.87 (q, 4-H) and 3.15 (s, <i>N-Me</i>)
17	8.20-7.00 (14H, m) and 6.70 (m, 4-H)
18	7.60-6.95 (13H, m), 6.15 (q, 4-H) and 3.25 (s, <i>N-Me</i>).

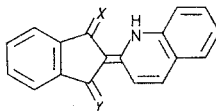
Table 1 contains p.m.r. data obtained for the anils and dianils and, for comparison, includes data for the *N*-methyl anil **16**, the anil **17** of 2-phenyl-1*H*-inden-1,3(2*H*)dione and the corresponding *N*-methyl anil **18**. The possibility of tautomerism arises with the anils and dianils. Pyrophthalone anil **10**, for example, has four possible tautomeric forms.

The compound in solution in chloroform exists predominantly in a keto form ($\nu_{C=O}$ 1670 cm⁻¹) and is hydrogen-bonded (δ 13.5, broad singlet) indicating forms **10a** or **b**. The presence of the absorption of the α -pyridinyl proton, H6', at δ 8.45 indicates that the aromaticity of the pyridine ring is intact. The chemical shift of the α -proton in the pyridinylideneimine tautomer **10a** would be expected to be considerably further upfield (ca. δ 7.3-7.5). Such an effect has been noted in several pyridinylidene systems^{6,7}. The p.m.r. spectrum of the *N*-methyl anil **16** is similar to that of the anil **10** as in the case of the 2-phenyl pair **17** and **18** (cf. ref.⁸).

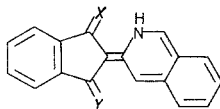
The p.m.r. spectra of the anils **11** and **12** each show signals attributable to a hydrogen-bonded NH group and to a shielded aromatic proton, H4. The coupling constant for H3' ($J_{3'4}$ 8.9 Hz) in compound **11** is closer to that reported for 2-acylquinolines which have been assigned the quinolinylidene structure⁹. The three dianils (**13**, **14**, and **15**) also show a chelated N—H absorption at δ 12.45–14.0 in the p.m.r. spectrum, and the α -pyridinyl proton H6' is at δ 8.76 in the spectrum of anil **14**.



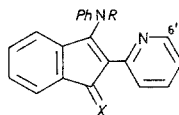
- 1 $X=Y=O$
 4 $X=S, Y=O$
 5 $X=Y=S$



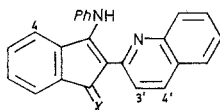
- 2 $X=Y=O$
 6 $X=S, Y=O$
 7 $X=Y=S$



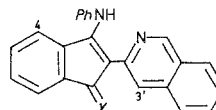
- 3 $X=Y=O$
 8 $X=S, Y=O$
 9 $X=Y=S$



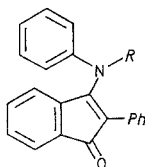
- 10 $X=O$ $R=H$
 14 NPh H
 16 O Me



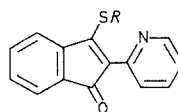
- 11 $X=O$
 15 NPh



- 12 $X=O$
 13 NPh



- 17 $R=H$
 18 Me



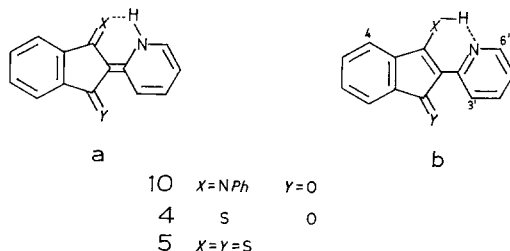
- 19 $R=Me$
 20 $benzyl$
 21 $allyl$

The tautomerism of pyrophthalone (**1**) and quinophthalone (**2**) has been extensively studied^{10–14}. In the case of monothiopyrophthalone (**4**) thioketo-thioenol tautomerism as well as ketoenol tautomerism is

Table 2. *Electronic spectra of Thiopyrophthalones 4 and 5 and their methyl-derivatives*

	$\lambda_{\max} (\epsilon) (\text{CHCl}_3) \text{ nm}$				
Monothiopyrophthalone (4)	312 (31 010)	340 (12 120) sh		402 (15 160)	464 (8 390)
Monothiopyrophthalone <i>N</i> -methyl ether	320 (22 680)			412 (13 970)	470 (8 380)
Monothiopyrophthalone <i>S</i> -methyl ether (19)	268 (17 360) sh	290 (20 430)		430 (2 380)	
Dithiopyrophthalone (5)	225 (11 840)	305 (22 190)	370 (19 260)	432 (15 349)	525 (5 560)
Dithiopyrophthalone <i>N</i> -methyl ether	250 (18 680)	308 (9 960)	370 (15 194)	420-490 br. sh.	525 (8 219)

possible. Table 2 shows the u.v.-visible spectrum of compound **4** compared with the data for the *N*-methyl-derivative and the *S*-methyl ether **19**. The spectrum of the *S*-methyl ether differs from the other two spectra suggesting that compound **4** exists predominantly in the pyridinylidene-thioketone form **4a** rather than the thioenol form **4b**. The similarity of the spectrum of the dithio-compound **5** and its *N*-methyl derivatives likewise indicates the predominance of tautomer **5a**. The fact that the p.m.r. spectra of compounds **1**, **4** and **5** show no absorption near δ 8.6 due to an α -pyridyl proton H6', is consistent with the loss of aromaticity⁶.



The sodium salt of pyrophthalone undergoes *N*-alkylation with dimethyl sulphate^{10,11} and alkyl halides¹⁵. In the case of monothiopyrophthalone reaction with dimethyl sulphate and methyl iodide under basic conditions each resulted in *S*-alkylation and formation of the methyl ether **19**. Similarly alkylation with benzyl chloride and allyl bromide in sodium hydroxide afforded the *S*-benzyl and *S*-allyl ethers

20 and **21**. The i.r. spectra of the three ethers showed $\nu_{C=O}$ (KBr) 1680-1690 cm^{-1} and the p.m.r. spectra showed the α -pyridinyl signal H6' at δ 8.75 (sextet). Aminolysis of the *S*-benzyl ether **20** afforded the *N*-methyl anil **16** which was inaccessible by treatment of pyrophthalone with *N*-methylaniline in presence of aluminium chloride or titanium chloride.

Table 3. *Spectroscopic data of metal complexes 22-28*

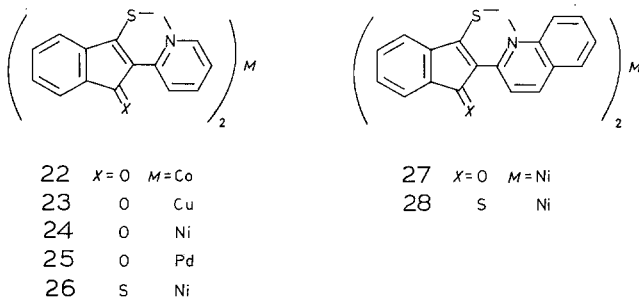
No.	ν_{max}		λ_{max} (CHCl_3) nm (ϵ)
22	1670	375	303 (42 100), 355 (s), (21 560), 465 (9 550)
23 *	1670	370 300	298 (35 975), 333 (48 170), 450 (9 450), 652 (200)
24	1670		295 (50 530), 340 (s) (28 790), 370 (26 150), 495 (8 520), 655 (100)
25	1660		310 (s) (38 600), 343 (45 130), 525 (13 060)
26			270 (42 350), 320 (36 670), 340 (s) (31 760), 390 (34 410), 565 (10 880), 600 (11 180), 708 (10 230)
27	1670		263 (43 780), 308 (51 350), 395 (27 570), 515 (6 750), 555 (5 950)
28			275 (49 680), 290 (s) (45 860), 345 (37 260), 405 (28 660), 567 (s) (9 550), 615 (11 150), 718 (7 320)

* E.s.r. (A) (satn. soln. in CHCl_3) g 2.07, a_{Cu} 65.7 G (4 lines), a_{N} 9.3 G (5 lines); (B) (solid spectrum) g 2.06 shoulder g 2.16.

The chelating tendencies of pyrophthalone (**1**)^{16,17} and quinophthalone (**2**)¹⁶ with bivalent metal ions have been reported. In both studies complexation in solution was determined and the chelates were not isolated. In contrast, monothiopyrophthalone (**4**) formed stable complexes of low solubility in organic solvents with Co(II), Cu(II), Ni(II) and Pd(II) (**22-25**) although the Pd(II) complex (**25**) was obtained in somewhat lower yield due to decomposition of the ligand in the refluxing solution of palladium(II) acetate. The Ni(II) complexes **26-28** were also readily isolated.

I.r. and u.v.-visible spectroscopic data for the complexes are given in Table 3. The spectrum of the Ni complex **24** shows a weak metal d-d transition at 655 nm (ϵ 100) which is consistent with a square planar structure; for the Cu complex **23** an absorption is observed at 652 nm (ϵ 200). The spectra of complexes **22-25** and **27** of the monothio-derivatives exhibit a carbonyl absorption of 1 670 cm^{-1} showing S $\rightarrow$ metal as opposed to O $\rightarrow$ metal complexation. The spectra recorded for CsBr discs show absorptions at 375 cm^{-1} for the

Co(II) chelate **22** and at 370 and 300 cm^{-1} for the Cu(II) chelate **23**. As the ligand does not absorb in this region these absorptions can be assigned to the $M-N$ and $M-S$ frequencies. In general ($M-S$) is reported¹⁸ to occur in the region 480–210 cm^{-1} and ($M-N$) over a wide range from 600 cm^{-1} to below 200 cm^{-1} and, specifically for pyridine, in the range 287– to below 200 cm^{-1} ¹⁹. No such absorptions however are apparent in the spectra of the Ni(II) and Pd(II) complexes **24** and **25**.



The Ni(II) complex **24** was found to be diamagnetic which is consistent with a square four covalent complex with a spin singlet ground state. The Co(II) complex **22** showed a temperature independent magnetic moment of 4.18 B.M. ($-150^\circ + 20^\circ \text{C}$). In a high spin tetrahedral complex of cobalt, the ground term is $4A_2$ and the moment is essentially the spin-only value of 3.88 B.N., with a temperature independent paramagnetism for high ligand field values — a value of 4.4–3.8 B.M. is normal. However, for a tetrahedral complex, a strong visible band (λ 600) would be expected. This is not observed so possibly an octahedral conformation is assumed in chloroform solution.

The e.s.r. spectrum of the Cu(II) chelate **23** in chloroform solution showed the hyperfine splitting (five peaks, 1:2:3:2:1) due to the coupling of two equivalent nitrogen atoms with the unpaired electron on the copper atom in a symmetrical environment. A similar spectrum has been reported for the chelate bis-(8-quinolinolato) Cu(II)²⁰. For steric reasons the *trans*-form of the bis-coordinate square planar complex would be expected. The e.s.r. spectrum of the complex **23** in the solid state is slightly asymmetrical, probably due to rhombic distortion of the square planar structure.

Experimental

N.m.r. spectra were recorded for solutions in CDCl_3 on Perkin-Elmer R 12 60 MHz (^1H n.m.r. spectra) and JEOL PFT 100 MHz (^1H and ^{13}C n.m.r. spectra) instruments; chemical shifts are in p.p.m. downfield from internal

SiMe_4 . I.r. spectra were recorded on Perkin-Elmer 237 and 125 spectrometers (1% in KBr discs) and, for the range $200\text{--}500\text{ cm}^{-1}$, on a Perkin-Elmer 457 spectrometer (2% in CsBr discs). U.v.-visible spectra were obtained for solutions in chloroform on Perkin-Elmer 124 and 402 spectrometers. E.s.r. spectra were recorded using a Decca X-1 spectrometer operating at 9.3 GHz with 100 GHz modulation. The g values were measured using Mn(II) as reference. Magnetic susceptibility measurements were obtained using a Newport Mk. II variable temperature Guoy balance (6,000 Gauss).

Preparative t.l.c. was carried out on Merck Kieselgel 60 $\text{PF}_{242+366}$ with benzene-ethyl acetate (9:1) as eluant. Merck silica gel 60/70-230 ASTM was used for column chromatography.

The anil **10** (79%) and **11** (85%) were prepared as previously described^{4,5}. The anil **10** has $\nu(\text{CHCl}_3)$ 1663 cm^{-1} and $\nu_{\text{C=O}}(\text{KBr})$ 1670 cm^{-1} ; $\lambda_{\text{max}}(\epsilon)$ 288 (25350), 340 (17320), 355 (13450) and 460 (4930).

Physical data for complexes **22–28** are tabulated.

N-Phenyl-3-phenylimino-2-(2-heteroaryl)-1*H*-inden-1-amines **14** and **15**

Titanium tetrachloride (10 ml) was added dropwise over 10 min to a suspension of compound **1** (6 g) in anhydrous benzene (500 ml) at reflux temperature. Aniline (15 ml) was added dropwise to the resulting suspension of the titanium complex. After 10 min the solvent was removed, water (200 ml) added to the residue and the mixture extracted with chloroform (200 ml). The extract was washed with water, dried and concentrated. The residue on crystallisation from ethanol gave the anil **14** as orange-red needles (9.6 g; 90%), m.p. $187\text{--}189^\circ\text{C}$ (Found: C 83.3, H 5.25, N 11.5. $\text{C}_{26}\text{H}_{19}\text{N}_3$ requires C 83.6, H 5.1, N 11.25%).

A solution of compound **2** (500 mg) in benzene (40 ml) treated as above with titanium chloride (2 ml) and aniline (3 ml) gave the "dianil" **15** as orange crystals (630 mg; 82%), m.p. $236\text{--}237^\circ$ (Found: C 85.5, H 5.3, N 9.9. $\text{C}_{30}\text{H}_{21}\text{N}_3$ requires C 85.1, H 5.0, N 10.0%).

3-Phenylamino-2-(2-isoquinolinyl)-1*H*-inden-1-one (**12**) and *N*-phenyl-3-phenylimino-2-(2-isoquinolinyl)-1*H*-inden-1-amine (**13**)

Aluminium chloride (300 mg) was added to a suspension of compound **3** (540 mg) in benzene (100 ml) at reflux temperature and heating continued for 15 min. Aniline (2 ml) was then added and the mixture was refluxed for a further 30 min. Water (100 ml) was cautiously added to the cooled mixture and the organic layer was separated, washed with water and dried. The solvent was evaporated off and the residue was separated by p.l.c. yielding two products. The compound of lower R_f value gave the anil **12** as red needles (306 mg; 44%) m.p. $204\text{--}205^\circ\text{C}$ (chloroform-hexane). The anil was analysed as the boron difluoride complex, orange needles m.p. $285\text{--}287^\circ$. (Found: C 72.3, H 3.9, N 7.0, F 9.95. $\text{C}_{24}\text{H}_{15}\text{BF}_2\text{N}_2\text{O}$ requires C 72.8, H 3.8, N 7.1, F 9.6%). The second product on crystallisation from chloroform-ethanol gave the dianil **13** as orange-brown plates (230 mg; 27%) m.p. $209\text{--}211^\circ\text{C}$ (Found: C 84.7, H 5.2, N 10.2. $\text{C}_{30}\text{H}_{21}\text{N}_3$ requires C 85.1, H 5.0, N 9.9%).

3-(*N*-Phenylmethylamino)-2-(2-pyridinyl)-1*H*-inden-1-one (**16**)

N-Methylaniline (0.11 ml) was added to a suspension of the *S*-benzyl ether **20** (312 mg) in ethanol (50 ml) and the mixture stirred for 1 h. The ethanol was removed and the residue on separation by p.l.c. gave the anil **16** which was

crystallised from chloroform-hexane in red needles (220 mg; 67%) m.p. 132–133 °C (Found: C 80.5, H 5.0, N 9.1. $C_{21}H_{16}N_2O$ requires C 80.75, N 5.2, N 9.0%); $[\lambda_{\max}(\epsilon)]$ 295 (20 700) and 447 (5 900); $\nu_{\max}$ 1 670 cm^{-1} (C=O). An unidentified yellow solid was also isolated.

3-(*N*-Phenylmethylamino)-2-phenyl-1*H*-inden-1-one (18)

A solution of 3-benzylthio-2-phenyl-1*H*-inden-1-one (250 mg) in *N*-methyl-aniline (5 ml) containing trichloroacetic acid (1 ml) was heated on a steam bath overnight. Chloroform (20 ml) was added and the organic solution was separated, washed with aqueous hydrogen chloride (10%; 20 ml) dried and evaporated. The residue was purified by p.l.c. and recrystallised from chloroform-hexane giving the *N*-methyl anil **18** (100 mg; 43%) m.p. 178–180 °C (Found: C 84.5, H 5.8, N 5.0. $C_{21}H_{15}NO$ requires C 84.5, H 5.5, N 4.5%); $\nu_{\max}$ 1 675 cm^{-1} (C=O); $\lambda_{\max}$ 287 and 358 nm.

General procedure for preparation of the monothio- and dithio-compounds 4–9

The anil or dianil was dissolved in the minimum amount of boiling ethanol to effect dissolution. Hydrogen sulphide was passed slowly through the solution, maintained at reflux temperature, until the starting material had reacted (t.l.c.), 8–16 h for the anils and 5–15 min for the dianils. The solution was allowed to cool, kept overnight and the crystalline product collected.

Compound 4, red crystals (93%) had m.p. 258 °C (lit.² m.p. 258 °C); δ 9.20 (m, 3'-H) and 7.0–8.3 (7 H, m).

Compound 5, purple needles (85%) had m.p. 238 °C (lit.² m.p. 238 °C); δ 10.2 (m, 3'-H) and 7.2–8.2 (7 H, m).

Compound 6, red crystals (93%) had m.p. 235–236 °C (lit.² m.p. 235–236 °C).

Compound 7, dark brown needles (72%) had m.p. 255–256° (lit.² m.p. 256 °C).

2,3-Dihydro-2-[3(2*H*)isoquinolinylidene]-3-thioxo-1*H*-inden-1-one (8)

Red crystals (73%) from chloroform-ethanol had m.p. 271–272 °C (Found: C 74.8, H 3.7, N 4.7, S 11.3. $C_{18}H_{11}NOS$ requires C 74.7, H 3.8, N 4.8, S 11.1%); $\nu_{C=O}$ 1 655 cm^{-1} .

2-[3(2*H*)Isoquinolinylidene]-1*H*-indene-1,3(2*H*)-dithione (9)

Purple needles (70%) from 1-nitropropane had m.p. 235–236 °C (Found: C 71.1, H 3.9, N 4.6, S 20.7. $C_{18}H_{11}NS_2$ requires C 70.8, H 3.6, N 4.6, S 21.0%).

3-Methylthio-2-(2-pyridinyl)-1*H*-inden-1-one (19)

(i) Methyl iodide (0.2 ml) was added to a solution of compound **4** (240 mg) in aqueous sodium hydroxide (5%; 50 ml) and the mixture stirred for 30 min. The resulting yellow precipitate was filtered off, washed with water and crystallised from ethanol giving the ether **19** as orange crystals (200 mg; 79%) m.p. 100–101 °C; δ 8.75 (sextet, 6'-H), 7.1–7.9 (7 H, m) and 2.40 (s, *S-Me*); ν 1 680 cm^{-1} (C=O); $\lambda_{\max}(\epsilon)$ 268 (s) (17 360), 290 (20 430) and 430 (2 380); (Found: C 71.6, H 4.2, N 5.9, S 12.25. $C_{15}H_{11}NOS$ requires C 71.1, H 4.4, N 5.5, S 12.7%).

(ii) A solution of compound **4** (240 mg), dimethyl sulphate (0.3 ml) and potassium carbonate (500 mg) in acetone (200 ml) was refluxed for 2 h. Work up afforded the thioether **19** (180 mg; 71%).

Table 4. *Physical data for complexes 22-28*

No.	Reaction solvent	Colour	Yield %	m.p. °C	Molecular Formula	Found % (Required %)			
						C	H	N	S
22	C ₂ H ₅ OH	brown	75	309-311 *	C ₂₈ H ₁₆ CoN ₂ O ₂ S ₂	62.85 (62.8)	3.0 3.0	5.4 5.2	12.5 12.0
23	C ₂ H ₅ OH	brown	70	> 350	C ₂₈ H ₁₆ CuN ₂ O ₂ S ₂	61.9 (62.3)	3.2 3.0	5.1 5.2	11.8 11.9
24	CHCl ₃ C ₂ H ₅ OH	purple	79	331-332 *	C ₂₈ H ₁₆ N ₂ NiO ₂ S ₂	62.6 (62.8)	3.05 3.0	5.3 5.2	11.8 12.0
25	C ₆ H ₆	purple	14	> 350 *	C ₂₈ H ₁₅ N ₂ O ₂ PdS ₂	57.4 (57.7)	3.0 2.8	5.3 4.8	10.7 11.0
26	C ₂ H ₅ OH	blue	49	328-329	C ₂₈ H ₁₆ N ₂ NiS ₄	59.6 (59.3)	3.0 2.8	5.0 4.9	23.0 22.6
27	C ₂ H ₅ OH	purple	75	> 350	C ₃₆ H ₂₀ N ₂ NiO ₂ S ₂	67.6 (68.1)	3.2 3.15	4.3 4.4	9.9 10.1
28	C ₂ H ₅ OH	green	75	> 350	C ₃₆ H ₂₀ N ₂ NiS ₄	65.0 (64.8)	3.1 3.0	4.2 4.2	19.1 19.2

* Recrystallised from C₂H₅OH—CHCl₃.

3-Benzylthio-2-(2-pyridyl)-1H-inden-1-one (**20**)

Benzyl chloride (0.5 ml) was added to a solution of monothioipyrophthalone **4** (240 mg) in aqueous sodium hydroxide (10%; 40 ml) and the solution was stirred overnight. The product was extracted into chloroform and the chloroform extract was dried and concentrated. The residue on crystallisation from chloroform-ethanol gave the thioether **20** as red needles (273 mg; 77%) m.p. 150-152 °C (Found: C 76.5, H 4.6, N 4.6, S 9.6. C₂₁H₁₅NOS requires C 76.6, H 4.6, N 4.25, S 9.7%); δ 8.77 (sextet, 6'-H), 7.0-7.8 (12 H, m) and 4.18 (2 H, s); $\nu_{\max}$ 1690 cm⁻¹ (C=O).

3-Allylthio-2-(2-pyridinyl)-1H-inden-1-one (**21**)

Allyl bromide (0.1 ml) was added to a solution of compound **4** (240 mg) in aqueous sodium hydroxide (10%; 40 ml) and the mixture stirred for 15 min. The resulting orange precipitate on recrystallisation from hexane gave the thioether **21** as orange plates (250 mg; 90%) m.p. 85-87 °C (Found: C 73.1, H 4.8, N 5.35, S 11.8. C₁₇H₁₃NOS requires C 73.1, H 4.7, N 5.0, S 11.5%); δ 8.75 (sextet, 6'-H), 7.1-7.9 (7 H, m) and 5.3-6.1 (1 H, m); $\nu_{\max}$ 1690 cm⁻¹ (C=O).

Preparation of the Complexes **22-26**

A freshly prepared solution of metal (II) acetate (0.5-2%; 1.4 mmol) was added to a refluxing solution of the ligand (0.2 mmol in 100-200 ml depending upon solubility). The solution was cooled and the complex collected. Solvents and yields are given in Table 4.

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