Melt syntheses of some [$PtCl_2L_2$] complexes

Duncan W. Bruce*, Bertrand Donnio, Andrew A. Maggs and Julian R. Marsden
Department of Chemistry, The University, Sheffield S3 7HF (U.K.)

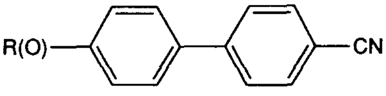
(Received February 14, 1991; revised May 24, 1991)

Abstract

Reaction of $PtCl_2$ in the melt of a ligand, L, leads in most cases to the complex [$PtCl_2L_2$] in good yield, with short reaction time. In all cases either pure *cis* or pure *trans* isomer is produced, depending on the nature of L.

Introduction

As part of our work on metal-containing liquid crystals [1], we synthesized a large family of complexes of the general formula *trans*-[MCl_2L_2] (M = Pd, Pt) where L was a mesogenic organonitrile of type **I**.



I

The palladium complexes were readily obtained in a simple substitution reaction between the ligand and [$PdCl_2(PhCN)_2$] in acetone at room temperature giving the pure *trans* isomer in good to moderate yield [2]. Initially, the analogous platinum complexes were obtained in a similar manner by reaction of *cis*-[$PtCl_2(PhCN)_2$] [3] with the ligand in refluxing toluene [2]. This again gave the pure *trans* isomer, but typically in yields of around 30–40% with some decomposition to platinum metal. These yields were not improved by use of the *trans* isomer of the starting material. Given the cost of platinum starting materials and also of the mesogenic ligands in which we were interested, it seemed appropriate to try to find an improved synthesis of these materials.

Experimental

Microanalysis was by the University of Sheffield Microanalytical Service. IR spectra were recorded between 4000 and 600 cm^{-1} on a Perkin-Elmer 1600 FT instrument and between 600 and 200 cm^{-1} on a Perkin-Elmer PE 684. All of the chemicals were used as supplied by the manufacturer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP80-SY instrument at 32.4 MHz with broad band proton decoupling.

Preparation of the complexes

All complexes were prepared in the same way according to the procedure exemplified by the formation of [$PtCl_2(7CB)_2$], although other solvent combinations were sometimes used to crystallise the complexes.

4-Heptyl-4′-cyanobiphenyl (7CB; 831 mg) was heated to 140 °C and $PtCl_2$ (269 mg) was added with stirring. The temperature was maintained for 30 min during which time the mixture solidified, turning yellow. After cooling to room temperature, the solid mixture was dissolved in chloroform and filtered twice through celite to remove unreacted $PtCl_2$, before a large excess of diethyl ether was added to precipitate the complex. The precipitated solid was recovered by centrifugation (this was found to be better than simple filtration) and then crystallised from chloroform/diethyl ether to give yellow crystals in 70% yield.

Yields and spectroscopic data for this and other complexes are presented in Table 1. The new complexes were also characterised by microanalysis (for which satisfactory C, H and halide percentages were obtained), while known complexes were characterised principally by their spectroscopic parameters.

Results and discussion

It has previously been reported [3] that a mixture of *cis*- and *trans*-[$PtCl_2(PhCN)_2$] could be obtained

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

TABLE 1. Yields and spectroscopic data for the complexes

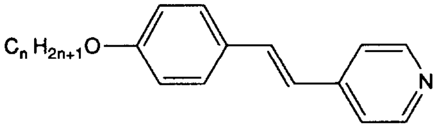
MX_2	Ligand	Yield (%)	ν(M–X) (cm^{-1})	ν(C≡N) (cm^{-1})	Geometry
$PtCl_2$	5CB	75	345	2295	*trans*
$PtCl_2$	7CB	73	345	2295	*trans*
$PtCl_2$	CCH5	67	345	2305	*trans*
$PtCl_2$	PCH5	51	345	2295	*trans*
$PtBr_2$	7CB	49	248	2290	*trans*
$PdCl_2$	7CB	15	370	2290	*trans*
$PtCl_2$	3-OPhVPy	56	350		*trans*
$PtCl_2$	12-OPhVPy	58	350		*trans*
PtI_2	3-OPhVPy	44			*trans*
$PtCl_2$	bipy	10	333, 295		*cis*
$PtCl_2$	PPh_3	57	310, 295	3673^{a}	*cis*
$PtCl_2$	$P(OPh)_3$	14	330, 305	3857^{a}	*cis*
$PtBr_2$	PPh_3	82	248, 240	3614^{a}	*cis*
PtI_2	PPh_3	63		2494^{a}	*trans*
$PdCl_2$	PPh_3	35	360		*trans*
$PtCl_2$	dppm	60^{b}		2025^{a}	

$^{a\,1}J$(Pt–P). ^{b}Yield of [Pt(dppm)$_2$]Cl$_2$.

by the direct reaction of $PtCl_2$ with PhCN and that the ratio of *trans/cis* increased with increasing temperature of the reaction. The two products were separated by column chromatography. Similarly the direct reaction between $[PtCl_4]^{2-}$ and MeCN to form *cis*- and *trans*-[PtCl$_2$(MeCN)$_2$] was reported [4] preferentially to give the *trans* isomer at higher temperatures.

Reasoning that similar conditions might lead to the formation of *trans*-[PtCl$_2$L$_2$] with improved efficiency, we maintained an isotropic melt of 6 equiv. of 4-pentyl-4′-cyanobiphenyl (5CB, colourless) at 140 °C and added to it 1 equiv. of $PtCl_2$ with stirring. Only half an hour later the mixture was yellow and had solidified, consistent with the formation of [PtCl$_2$(5CB)$_2$]. Work-up of this solid showed that we had indeed obtained pure *trans*-[PtCl$_2$(5CB)$_2$] in a recovered yield of about 70%. Further optimisation of this system showed that the same results could be obtained using only 3 mol equiv. of 5CB as solvent (i.e. only one mole excess) with a small reduction in yield. Given the cost of the ligand, this represents a more effective way of generating the complex. The *trans* geometry about the metal centre was confirmed by IR and NMR spectroscopy (see 'Experimental') and by comparison of the liquid crystal behaviour with an authentic sample whose *trans* geometry had been confirmed by single crystal X-ray analysis [2]. The same reaction was then carried out with the related ligands CCH5 (4-pentyl-*trans,trans*-bicyclohexyl-4′-carbonitrile) and PCH5 (4-pentyl-*trans*-cyclohexyl-4′-cyanophenyl) and again, pure *trans* complexes were obtained in comparable recovered yields.

Similarly, the reaction produced the *trans* isomer in around 50–60% recovered yield using mesogenic 4-alkyloxy-4′-stilbazoles [5] (n-OPhVPy) (**II**). This reaction is then a quick, convenient route into pure *trans* complexes of mesogenic N-donor ligands.



II

This reaction was then attempted using $PdCl_2$, $PtBr_2$ and PtI_2 using a reduced selection of ligands and a standard set of conditions as described in 'Experimental'. For $PdCl_2$, the reaction worked well for the alkyloxystilbazoles (yields ≈75%), but for the cyanobiphenyls the recovered yields were much reduced (≈15%). This is due to the lability of these complexes in solution which becomes a problem during recrystallisation [6]. (Bailey *et al.* [6] describe the lability of [PdCl$_2$(PhCN)$_2$].) Both $PtBr_2$ and PtI_2 gave moderate yields (≈50%) of the *trans* complexes with the stilbazole ligand, but whereas $PtBr_2$ gave 50% of [PtBr$_2$L$_2$] with cyanobiphenyl, PtI_2 appeared to give no reaction. Given the inertness of Pt–I bonds and the fact that a reaction of this type would have to break up an extended Pt–I–Pt network, we explain this lack of reaction in terms of the limited donor strength of organonitriles compared with the more basic pyridine derivatives.

To see if such a method was more generally applicable, the reaction was then carried out with a wider variety of ligands, including chelating ligands for which a *cis* geometry was the only possibility.

Using triphenylphosphine, moderate to good yields were obtained with the full range of salts studied, except that for platinum the complexes were now *cis* (with the exception of [$PtI_2(PPh_3)_2$] which was *trans*) as shown by ^{31}P NMR and IR spectroscopy and by the colour of the complexes. Triphenylphosphite gave unoptimised yields of the *cis* complex of only 14%. Reaction of $PtCl_2$ with 3 equiv. of the bidentate phosphine dppm did not stop at [$PtCl_2$(dppm)] but continued to give [Pt(dppm)$_2$]Cl_2 in moderate yield ($\approx$50–60%; ^1J(Pt–P)($CDCl_3$) = 2025 Hz [7]). The same reaction using 1.5 equiv. (i.e. 3 phosphorus/Pt) gave a mixture of materials.

The use of other N-donor ligands in this reaction was disappointing. Thus, alkylamines and alkylanilines gave some *trans* product in very low yield ($\approx$5–10%), while reaction with 2,2′-bipyridyl at 140 °C for 3 h gave [$PtCl_2$(bipy)] in about 10% yield. No reaction was obtained for 1,10-phenanthroline under the same conditions.

Conclusions

For the mesogenic nitrogen-donor listed above, this reaction represents an efficient and quick route into pure *trans* complexes of Pt(II), while for other ligands the yields were less satisfactory; in all cases, only one geometric isomer was obtained making purification much easier. Proper optimisation of the conditions of this reaction for different ligands will allow this route to be tailored to specific requirements.

Acknowledgements

We acknowledge support from the Royal Society (D.W.B.) and the EC ERASMUS programme (B.D.) and J.R.M. thanks the SERC and Johnson Matthey for a CASE Studentship. Generous loans of platinum dihalides from Johnson Matthey are gratefully acknowledged. Anna Thornton is thanked for recording ^{31}P NMR spectra.

References

1 D. W. Bruce, D. A. Dunmur, S. E. Hunt, R. Le Lagadec, P. M. Maitlis, J. R. Marsden, J. M. Stacey, M. A. Esteruelas and E. Sola, *J. Mater. Chem.*, *1* (1991) 251; D. W. Bruce, D. A. Dunmur, M. R. Manterfield, P. M. Maitlis and R. Orr, *J. Mater. Chem.*, *1* (1991) 255; C. Bertram, D. W. Bruce, D. A. Dunmur, S. E. Hunt, P. M. Maitlis and M. McCann, *J. Chem. Soc., Chem. Commun.*, (1991) 69.

2 D. W. Bruce, E. Lalinde, P. Styring, D. A. Dunmur and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1985) 581; H. Adams, N. A. Bailey, D. W. Bruce, D. A. Dunmur, E. Lalinde, M. Marcos, C. Ridgway, A. J. Smith, P. Styring and P. M. Maitlis, *Liq. Cryst.*, *2* (1987) 381.

3 T. Uchiyama, Y. Toshiyasu, Y. Nakamura, T. Miwa and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, *54* (1981) 181.

4 F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Chem. Soc., Dalton Trans.*, (1990) 199.

5 D. W. Bruce, D. A. Dunmur, E. Lalinde, P. M. Maitlis and P. Styring, *Liq. Cryst.*, *3* (1988) 385.

6 D. W. Bruce, D. A. Dunmur, S. E. Hunt, P. M. Maitlis, R. Orr and P. Styring, unpublished results; P. M. Bailey, E. A. Kelley and P. M. Maitlis, *J. Organomet. Chem.*, *144* (1978) C52.

7 M. C. Grossel, R. P. Moulding, K. R. Seddon and F. J. Walker, *J. Chem. Soc., Dalton Trans.*, (1987) 705.