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Synthesis and Reactions with Iodine of Trialkylphosphine- or γ-Picoline-bis(N-alkyldithiocarbamate)platinum(II) Complexes

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It is well known [1–6] that square-planar $|M(S–S)_2|$ complexes [M = Ni, Pd or Pt; $(S–S)^-$ = $(S_2PR_2)^-$, $(S_2CNR_2)^-$, $(S_2COR)^-$ or $(S_2P(OR)_2^-$ react with various tertiary phosphines to give the unsymmetrical four-coordinate square-planar complexes $|M(S–S)_2L|$ and $|M(S–S)L_2|^+|S–S|^-$.

As far as we know, no evidence appears in the literature on the reactions of bis(N-alkyldithiocarbamate)platinum(II) complexes with tertiary phosphines or nitrogenous bases.

In the present paper we report our preliminary results on the synthesis of tricyclohexylphosphine or γ-picoline-bis(N-benzyldithiocarbamate)platinum(II) complexes, as well as their reactions with iodine.

Experimental

Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 467 spectrophotometer using KBr discs.

^{1}H n.m.r. spectra were recorded on a Varian A 60A (60 Mc/s) instrument in $CDCl_3$ or $(CD_3)_2SO$ solutions using TMS as internal standard.

The determination of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240 Elemental Analyser.

Preparation of the Complexes

The bis(N-benzyldithiocarbamate)platinum(II), $Pt(S_2CNHBz)_2$, was prepared by the addition of CS_2 (4 mmol) and $BzNH_2$ (8 mmol) to a suspension of $PtCl_2$ (2 mmol) in $CHCl_3$, under continuous magnetic stirring at room temperature. The yellow precipitate formed was filtered, washed with ethanol and dried under vacuum (yield: 82%).

The bis(N-benzyldithiocarbamate)tricyclohexylphosphineplatinum(II), $Pt(S_2CNHBz)_2PCy_3$, was prepared by the addition of a solution of PCy_3 (0.5 mmol) in absolute ethanol to a suspension of $Pt(S_2CNHBz)_2$ (0.5 mmol) in toluene, under nitrogen atmosphere. In the resulted clear solution the desired complex was appeared as a pale-yellow precipitate which was filtered off, washed with ethanol and dried under vacuum (yield: 70%). It must be noted that following the same route, but using an excess of phosphine, the same compound was isolated.

The bis(N,N-diethyldithiocarbamate)tricyclohexylphosphineplatinum(II), $Pt(S_2CNEt_2)_2PCy_3$, was prepared in a similar manner (yield: 73%).

The bis(N-benzyldithiocarbamate)γ-picolineplatinum(II), $Pt(S_2CNHBz)_2$ (γ-pic), was prepared by the addition of an excess of γ-picoline to a suspension of $Pt(S_2CNHBz)_2$ (0.5 mmol) in toluene at room temperature. In the resulting clear solution petroleum ether was added and a yellow precipitate was formed, which was filtered off and dried under vacuum (yield: 69%).

The iodo(N-benzyldithiocarbamate)tricyclohexylphosphineplatinum(II) $Pt(S_2CNHBz)(PCy_3)I$, was prepared by the addition of iodine (0.25 mmol) dissolved in toluene to a suspension of $Pt(S_2CNHBz)_2PCy_3$ (0.5 mmol) in the same solvent. An orange solid was precipitated which was filtered off, washed with petroleum ether and dried under vacuum (yield: 74%).

The same synthetic route was followed for the preparation of the complexes $Pt(S_2CNHBz)(\gamma\text{-pic})I$ and $Pt(S_2CNEt_2)(PCy_3)I$. The yields were 78% and 69%, respectively.

Results and Discussion

In Table I are listed the analytical and the most characteristic spectral data for the new complexes.

All the compounds are monomeric in solution, diamagnetic and stable in air, except the complex $Pt(S_2CNHBz)_2(\gamma\text{-pic})$ which loses readily the γ-picoline molecule. The instability of this complex may be due either to the high electron density on the central atom in the dithiocarbamate complexes or to the absence of π-acid character of γ-picoline. The π-acid character of the phosphines is the most important factor for the stability of their adducts with the square-planar $[M(S–S)_2]$ complexes.

Considering the stronger electron releasing ability of the N,N-diethyldithiocarbamato ligand than the N-benzyldithiocarbamato, we should expect the less stability of the γ-picoline adduct with the former. This was confirmed, for though we tried to prepare the bis(N,N-diethyldithiocarbamate)γ-picolineplatinum(II), our efforts were unsuccessful. With respect to this, we may say that N-alkyldithiocarbamate complexes have a similar behaviour to the xanthates, which form stable adducts with nitrogenous bases, than to the N,N-dialkyldithiocarbamates. However, with respect to the reactions of N-alkyldithiocarbamates with excess of phosphine, they have a closer behaviour to the N,N-dialkyldithiocarbamates than

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TABLE I. Analytical and Spectral Data.

Compound	% C	% N	% H	% Pt	I.r. Frequencies $\nu(C\underline{\cdot\cdot}N)$	$(cm^{-1})^b$ $\nu(N–H)$	^1H N.m.r Chemcial Shifts (τ, ppm)^c
$Pt(S_2CNHBz)_2$	34.31	4.92	2.85	34.2	1540 (vs)	3260 (vs)	2.62 s; 5.45 s
	(34.34)^a	(5.00)	(2.88)	(34.8)			
$Pt(S_2CNHBz)_2(PCy_3)$	48.97	3.21	6.18	22.9	1535 (vs)	3300 (m)	2.64 s; 5.30 s; 7.86–9.00 br
	(48.61)	(3.33)	(5.88)	(23.2)	1490 (s)	3130 (m)	
$Pt(S_2CNHBz)(PCy_3)I$	39.71	1.69	5.36	24.6	1532 (vs)	3140 (m)	2.62 s; 5.35 s; 7.88–8.85 br
	(39.79)	(1.78)	(5.26)	(24.8)			
$Pt(S_2CNHBz)_2(\gamma$-pic)	40.26	6.34	3.51	29.6	1520 (vs)	3250 (m)	2.64 s; 5.35 s; 7.65 s
	(40.48)	(6.44)	(3.55)	(29.8)	1488 (m)	3150 (m)	
$Pt(S_2CNHBz)(\gamma$-pic)I	28.09	4.64	2.58	32.2	1525 (vs)	3220 (s)	2.65 s; 5.40 s; 7.66 s
	(28.15)	(4.69)	(2.53)	(32.6)			
$Pt(S_2CNEt_2)_2(PCy_3)$	43.48	3.65	6.99	24.9	1520 (vs)		6.25 q; 8.70 t; 7.88–8.42 br
	(43.56)	(3.63)	(6.92)	(25.2)	1445 (vs)		
$Pt(S_2CNEt_2)(PCy_3)I$	(36.75)	(1.84)	5.85	25.8	1518 (vs)		6.39 q; 8.70 t; 7.88–8.30 br
	36.79	1.88	(5.77)	(25.9)	1445 (vs)		

^{a}Figures in parentheses are the calculated values. ^{b}In KBr discs. ^{c}In d_6-DMSO solutions.

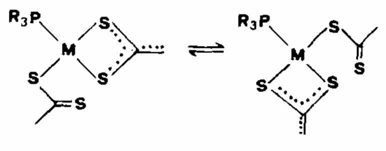
to the xanthates. Thus, no dithioiminocarbonato complexes are formed by nucleophilic attack of the ionic N-alkyldithiocarbamato group on a coordinated alkylamino group of the complex $[M(S_2CNHBz)(PCy_3)_2]^+[S_2CNHBz]^-$, in contrast to the xanthates which give the dithiocarbonato complexes [2, 3, 7].

The complexes $M(S–S)_2L$ (where $(S–S)^-$=$Et_2NCS_2^-$, $BzHNCS_2^-$, and L=PCy_3 or γ-pic) were found to react easily with iodine to give the corresponding unsymmetrical square-planar complexes M(S–S)LI, according to the reaction:

$$M(S–S)_2L + 1/2I_2 \rightarrow M(S–S)LI + 1/2(S–S)_2$$

This reaction is a very simple general synthetic route of the M(S–S)LI complexes, which can be also prepared in one step by adding to a solution of the dithiocarbamate complex in toluene the phosphine or the γ-picoline, followed by the addition of the halogen. These complexes are very interesting because they give a number of important reactions. Thus, they react with carbene like molecules, such as SnX_2, to give the insertion products into the Pt–I bond which contain Pt–Sn bonds. They also give a number of substitution reactions of the iodide with other nucleophiles. The study of these reactions for a number of M(S–S)LI complexes is in progress and full results will be published soon.

The structures of the complexes were established by spectroscopic methods. Only one broad band, due to the N–H stretching frequency, was observed in the $M(S_2CNHBz)_2$ and $M(S_2CNHBz)LI$ complexes. This is an indication for the equivalence of the two $BzHNCS_2^-$ ligands. The bidentate character of these ligands was established by the position of the band which is due to the stretching frequency of the partial double bond $C\underline{\cdot\cdot\cdot}N$. On the contrary, the $\nu(N–H)$ band is split into two sharp bands, in the $M(S_2CNHBz)_2L$ complexes. This fact indicates the coexistence of two different kinds of $BzHNCS_2^-$ ligands, one acting as bidentate and the other as unidentate. The coexistence of such ligands was also established by several authors [2]. In $CHCl_3$ solution, however, the two $BzHNCS_2^-$ ligands become equivalent. This may be due to the dynamic behaviour of the fluxional $M(S_2CNHBz)_2L$ complexes, which can be represented by the following scheme.



This in accordance with the suggestions of other authors about the dynamic behaviour of analogous compounds [2, 8].

References

1 J. M. C. Alison, T. A. Stephenson and R. O. Gould, *J. Chem. Soc. A, 3690 (1971).*
2 J. M. C. Alison and T. A. Stephenson, *J. Chem. Soc. Dalton*, 254 (1973).
3 J. P. Fackler, Jr., W. C. Seidel and J. A. Fetchin, *J. Am. Chem. Soc., 90*, 2707 (1968).
4 J. P. Fackler, Jr., J. A. Fetchin and W. C. Seidel, *J. Am. Chem. Soc., 91*, 1217 (1969).
5 J. P. Fackler, Jr., W. C. Seidel, *Inorg. Chem., 8*, 1631 (1969).
6 J. Zagal and J. A. Costamagna, *Inorg. Nucl. Chem. Letters, 13*, 411 (1977).
7 M. C. Cornock, R. O. Gould, C. L. Jones, J. O. Owen, D. F. Steele and T. A. Stephenson, *J. Chem. Soc. Dalton*, 496 (1977).
8 M. C. Cornock and T. A. Stephenson, *J. Chem. Soc. Dalton*, 501 (1977).