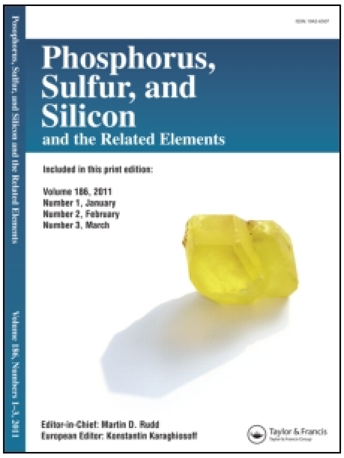


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE SYNTHESIS OF TRISELENOCARBONATE COMPLEXES OF PLATINUM

Stephen M. Aucott[a]; Colin J. Burchell[a]; Alexandra M. Z. Slawin[a]; J. Derek Woollins[a]
[a] University of St. Andrews, Fife, Scotland

To cite this Article Aucott, Stephen M. , Burchell, Colin J. , Slawin, Alexandra M. Z. and Woollins, J. Derek(2004) 'THE SYNTHESIS OF TRISELENOCARBONATE COMPLEXES OF PLATINUM', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 903 — 906

To link to this Article: DOI: 10.1080/10426500490428870

URL: http://dx.doi.org/10.1080/10426500490428870

Phosphorus, Sulfur, and Silicon, 179:903–906, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490428870

THE SYNTHESIS OF TRISELENOCARBONATE COMPLEXES OF PLATINUM

Stephen M. Aucott, Colin J. Burchell Alexandra M. Z. Slawin, and J. Derek Woollins
University of St. Andrews, Fife, Scotland

(Received August 18, 2003; accepted October 3, 2003)

The addition of dichloromethane solutions of carbon diselenide to liquid ammonia containing suspensions of platinum bis-phosphine dichlorides $[PtCl_2(PR_X)_n]$ *(n = 2,* $(PR_X) = PMe_3, PMe_2Ph, PMePh_2$*, and* PPh_3*, n = 1,* (PR_X) *= dppm, dppe, dppp, dppf) gives, after evaporation of the ammonia and extraction of the reaction residues with dichloromethane, the appropriate platinum bis-phosphine triselenocarbonate complexes in reasonable yields (40–60%).*

Keywords: Bidentate; carbon diselenide; complexes; metallacycles; triselenoarbonate

The carbonate $[CO_3]^{2-}$ dianion **A** (Figure 1) is the most common and perhaps the most important of all the known oxoanions of carbon. This is reflected in the number of known complexes and materials which appear in the chemical literature. The carbonate dianion also exhibits many binding modes in its coordination chemistry. Its sulfur analogue trithiocarbonate $[CS_3]^{2-}$ **B** is considerably less common in terms of both the number of known compounds and different binding modes. Rarer still is the triselenocarbonate $[CSe_3]^{2-}$ dianion **C** of which to the best of our knowledge there is only a single literature example.

Carbon disulfide (CS_2) has been used to great effect in the preparation of a number of di-sulfur donor ligands (Figure 2). Reaction of CS_2 with cyanimide (in the presence of base) with, secondary amines, alkoxides, and alkali metal hydroxides in polar solvents give, respectively,

---

We are grateful to the EPSRC (S.M.A.) for funding and to the JREI for an equipment grant.

Address correspondence to J. Derek Woollins, Department of Chemistry, University of St. Andrews, Fife KY16 9ST, Scotland. E-mail: JDW3@st-andrews.ac.uk

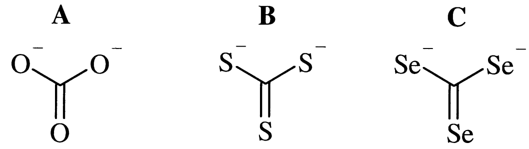
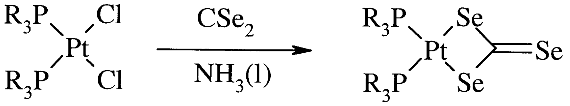


FIGURE 1 Sulfur and selenium analogs of the carbonate anion.

the bidentate disulfur ligands cyanimidodithiocarbonates **D**, dithiocarbamates **E**, dithioxanthogenates **F**, and the trithiocarbonate dianion **G**[1] respectively. It also is well established that substitution of CSe_2 for CS_2 in these reaction leads to the diseleno analogues of **D**,[2] **E**,[3] and **F**.[4] This is not the case for reaction **G** where using carbon diselenide under the same reaction conditions yields only polymeric material. The absence of a synthetic method for the generation of the triselenocarbonate dianion has meant that at present there is only a single literature example of a monomeric complex containing this ligand $[(\eta{-}^5C_5H_5)Co(CSe_3)(PMe_3)]$, this was formed as a reaction bi-product and isolated in only 7% yield.[5]

RESULTS AND DISCUSSION

Recently we reported an alternative method for the preparation of trithiocarbonate complexes of platinum and palladium using liquid ammonia as the basic medium to produce $[CS_3]^{2-}$.[6] We have since found that under that same reaction conditions using CSe_2 we can isolate triselenocarbonate complexes of platinum (Eq. 1).



(1)

The $^{31}P\{^1H\}$ NMR spectra of the $[Pt(CSe_3)(PR_X)_n]$ complexes are very similar in terms of both $\delta(P)$ and $^1J(^{31}P\text{-}^{195}Pt)$ values but have additional ^{77}Se satellites with $^2J(^{31}P\text{-}^{77}Se)$ couplings of typically 25 Hz. In

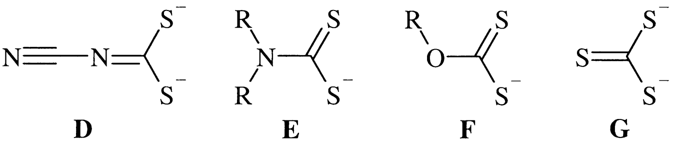


FIGURE 2 Di-sulfur ligands prepared from carbon disulfide.

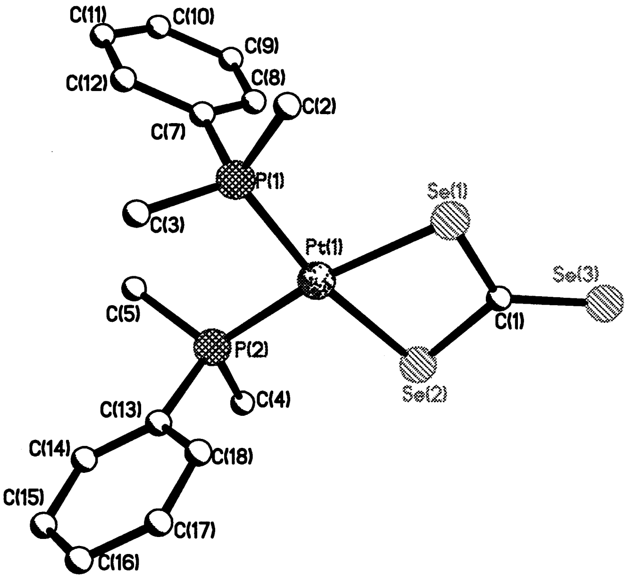


FIGURE 3 Crystal structure of $[Pt(CSe_3)(PMe_2Ph)_2]$.

some examples two sets of ^{77}Se satellites are observed with $^2J(^{31}P\text{-}^{77}Se)$ couplings of 20 and 30 Hz which we believe are *cis* and *trans* $^2J(^{31}P\text{-}^{77}Se)$ couplings. The ν(C=Se) vibrations are observed at ca. 900 cm^{-1} and the ν(Pt—Se) bands are in the region 350–398 cm^{-1}. The crystal structure of $[Pt(CSe_3)(PMe_2Ph)_2]$ has been determined and shows the platinum centre exhibits distorted square planer geometry (Figure 3). The Pt—Se 2.456(1) and 2.563(1), Se—C 1.860(13) and 1.884(13), and the C=Se 1.794(13) distances are significantly longer than those found in the corresponding CS_3 complex.

Although in most cases the dichloromethane soluble component of the reaction residue constitutes a single species the use of $[PtCl_2(PEt_3)_2]$ in this reaction system gives two major products. The first is the anticipated mononuclear species $[Pt(CSe_2)(PEt_3)_2]$ the second is the highly unusual tetrameric species $[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$ which was deposited as large red crystals from chloroform. The structure shows the molecue consists of four $[Pt(CSe_3)(PEt_3)]$ repeat units and that each platinum atoms lie in distorted square planar coordination sphere consisting of a PEt_3 ligand two ring selenium atoms and an exocyclic selenium atom from an adjacent monomeric unit (Figure 4). The molecule is in a tetragonal space group P-42(1)c and has crystallographic four fold symmetry.

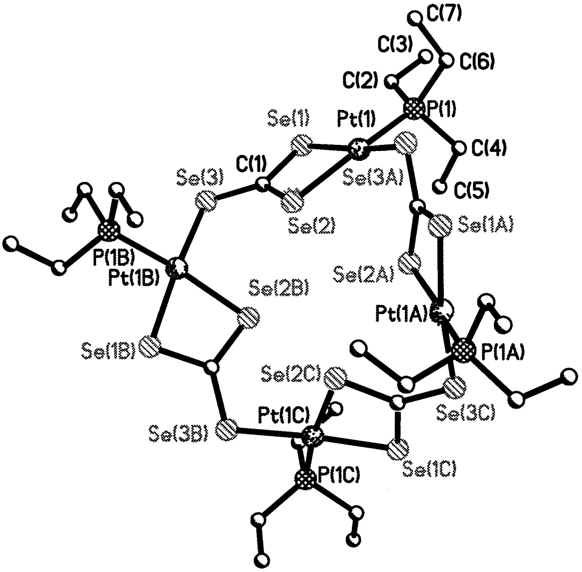


FIGURE 4 Crystal structure of [{Pt(μ-CSe$_3$)(PEt$_3$)}$_4$].

CONCLUSIONS

Triselenocarbonate complexes are accessible via a straightforward (one-pot) synthetic route by adding CSe$_2$ to [PtCl$_2$(PR$_X$)$_n$] suspensions in liquid ammonia giving in most examples so far attempted single species which are easily isolable.

REFERENCES

[1] J. P. Fackler Jr. and D. Coucouvanis, *J. Am. Chem. Soc.*, **88,** 3913 (1966).
[2] K. Jensen and L. Henriksen, *Acta. Chem. Scand.*, **24,** 3213 (1970).
[3] D. Bernard and D. T. Woodbridge, *J. Chem. Soc.*, 2922 (1961).
[4] A. Rosenbaum, H. Kirchberg, and E. Leibnitz, *J. Prakt. Chem.*, **19,** 1 (1963).
[5] O. Kolb and H. Werner, *J. Organomet. Chem.*, **268,** 49 (1984).
[6] S. M. Aucott, A. M. Z. Slawin, and J. D. Woolins, *Polyhedron*, **19,** 499 (2000).