transition-metal ion. These complexes generally have a saddle shape which is attributed to steric interactions between the aromatic rings and the methyl groups. A planar structure was found in one case where the methyls are absent.[17] Bond lengths found for the β-diiminate portions of the macrocyclic ligand in complex II are very close to those reported for complexes III. For example, C⋯N, C⋯C, and C—CH_3 bond lengths for III fall in the ranges 1.31–1.35 Å, 1.38–1.41 Å, and 1.49–1.52 Å, respectively.[15-19] Bond angles for II are also close to those observed for III except for the Au—N⋯C angles which are 2–6° smaller.

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Registry No. II·Cl·$2H_2O$, 76037-14-4.

Supplementary Material Available: Table V containing observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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(16) Goedken, V. L.; Peng, S. M.; Molin-Norris, J.; Park, Y. *J. Am. Chem. Soc.* **1976**, *98*, 8391–8400.

(17) Weiss, M. C.; Gordon, G.; Goedken, V. L. *Inorg. Chem.* **1977**, *16*, 305–310.

(18) Weiss, M. C.; Goedken, V. L. *Inorg. Chem.* **1979**, *18*, 274–279.

(19) Weiss, M. C.; Goedken, V. L. *Inorg. Chem.* **1979**, *18*, 819–826.

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Preparations and ^1H, ^{13}C, and ^{31}P Nuclear Magnetic Resonance Studies of Some *N*,*N*-Dialkyldiselenocarbamate Complexes and Their Phosphine Derivatives. X-ray Crystal Structure of $Pt(Se_2CN(i\text{-}Bu)_2)_2$

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A convenient synthesis of CSe_2 is reported which can be used to prepare dialkyldiselenocarbamates. The ^1H, ^{13}C, and ^{31}P NMR spectra of about 25 derivatives containing the metal ions Zn(II), Ni(II), Pd(II), Pt(II), Pt(IV), and Co(III) are reported. The single-crystal X-ray structure of monoclinic $Pt(Se_2CN(i\text{-}Bu)_2)_2$ (a = 6.736 (1) Å, b = 12.357 (2) Å, c = 15.496 (4) Å, β = 99.03 (2)°) establishes the coordination geometry to be the same as that found[1] for the $Pt(S_2CNEt_2)_2$ analogue. The average Pt–Se distance is 2.427 (3) Å, an increase of ~0.11 Å over the Pt–S distance, similar to the increase observed for Ni–Se over Ni–S.

While the chemistry of the dithiocarbamates[1] began back in the middle 1800s, the chemistry of the diselenocarbamates is of more recent origin. The preparation of CSe_2 was reported in as early as 1936 by Grimm and Metzger,[2] but it was not until in 1961 that Barnard and Woodbridge[3] described the first preparations of the sodium salts and zinc and copper complexes of dialkyldiselenocarbamic acids, using CSe_2 as one of the starting materials. Apparently, this delay in the development of the chemistry of the diselenocarbamates is due to the toxicity[4] and unpleasant odor associated with CSe_2 (and selenium compounds in general[4,5]), rendering it difficult to handle. It was also noted[3,6] that unlike CS_2, CSe_2 polymerizes readily, particularly in the presence of base, making it useless for the preparation of the diselenocarbamate salt by reaction with amines. An additional drawback is the generally low yield encountered in the preparation of CSe_2 by using the early methods of Grimm and Metzger[2] and Ives et al.[6]

The development[7,8] of ^{77}Se NMR has prompted our studies of the selenium analogues of metal dithiocarbamates. Much spectroscopic data (IR,[9,10] UV–vis[10]) as well as a few crystal structures[11] of *N*,*N*-dialkyldiselenocarbamate complexes have been reported. There is, however, a scarcity of NMR data[12] on these types of complexes. In the course of our study, some interesting multinuclear (^1H, ^{13}C, and ^{31}P) NMR results have been obtained. Also a small scale (~20 g) convenient synthesis of CSe_2, with yields upward of 80%, has been devised. This method is a simplified version of the one reported by Henriksen and Kristiansen[13] for preparing CSe_2 on a larger scale (800 g). The structure of $Pt(Se_2CN(i\text{-}Bu)_2)_2$, synthesized from CSe_2, also is described here.

Experimental Section

Preparation of Compounds. Reagent grade solvents were used unless otherwise stated. The compounds $MCl_2(PR_3)_2$ (M = Ni, Pd, Pt)[14,15] and *cis*-$Pt(CH_3)_2(PPh_3)_2$[16] were prepared according to literature methods. K_2PdCl_4 and K_2PtCl_4 were prepared from the respective metals, the former following the method of Kauffman and Tsai[17] for Na_2PdCl_4 and the latter according to Brauer.[18] All chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. (Table I).

Carbon Diselenide. Figure 1 is a diagram of the apparatus used. Grey Se powder (16–22 g) in a quartz boat (14 × 1.5 cm) is placed

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(1) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 234–371; **1979**, *26*, 302–451.

(2) Grim, H. G.; Metzger, H. *Chem. Ber.* **1936**, *69*, 1356.

(3) Barnard, D.; Woodbridge, E. T. *J. Chem. Soc.* **1961**, 2922.

(4) Sax, N. I. "Dangerous Properties of Industrial Materials", 2nd ed.; Reinhold: New York, 1963; p 575.

(5) "Organic Selenium Compounds: Their Chemistry and Biology"; Klayman, D. L., Günther, W. H. H., Eds.; Wiley-Interscience: New York, 1973.

(6) Ives, D. J. G.; Pittman, R. W.; Wardlaw, W. *J. Chem. Soc.* **1947**, 1080.

(7) Pan, W.-H.; Fackler, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 5783. Harris, R. K.; Mann, B. E. "NMR and the Periodic Table"; Academic Press: New York, 1978; Chapter 12.

(8) Fackler, J. P.; Pan, Wie-Hin *J. Am. Chem. Soc.* **1979**, *101*, 1607.

(9) Jensen, K. A.; Krishnan, V. *Acta Chem. Scand.* **1969**, *24*, 1088.

(10) (a) DeFilipo, D.; Deplan, P.; Diaz, A.; Trogu, E. F. *Inorg. Chim. Acta* **1976**, *17*, 139. (b) DeFilipo, D.; Deplano, P.; Devillanova, F.; Trogu, E. F. *Ibid.* **1976**, *17*, 199. (c) Mannoussakis, G. E.; Tsipis, C. A.; Chirstophides, A. G. *Inorg. Chem.* **1973**, *12*, 3015.

(11) Bonamico, M.; Dessy, G. *J. Chem. Soc. A* **1971**, 264.

(12) Tanaka, T.; Sonoda, N. *Inorg. Chem.* **1971**, *10*, 2337.

(13) Henriksen, L.; Kristiansen, E. S. S. *Int. J. Sulfur Chem. Part A* **1972**, *2*, 133.

(14) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 770.

(15) Cousmaker, C. R.; Hely-Hurchinson, M.; Mellor, J. R.; Sutton, L. E.; Venanzi, L. M. *J. Chem. Soc.* **1961**, 2705.

(16) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705.

(17) Kauffman, G. B.; Tsai, J. H.-S. *Inorg. Synth.* **1966**, *8*, 234.

(18) Brauer, G. "Handbook of Preparative Inorganic Chemistry"; Academic Press: New York, 1965; Vol. 2, p 1572.

0020-1669/81/1320-0856$01.00/0

Table I. Analytical Results and Melting Points

			% calculated				% found			
compd	color	mp, °C	C	H	N	Se	C	H	N	Se
Zn(Se$_2$CNEt$_2$)$_2$	light yellow	152–154	21.86	3.64	5.10	57.50	21.9	3.8	5.2	57.8
Zn(Se$_2$CN(*i*-Bu)$_2$)$_2$	off white	137–139	32.67	5.49	4.23		32.7	5.7	4.1	
Ni(Se$_2$CN(*i*-Bu)$_2$)$_2$	olive green	170–173	33.00	5.50	4.28	48.22	32.7	5.5	4.2	48.5
Ni(Se$_2$CNEt$_2$)PEt$_3$Cl	dark red	93–95	29.08	5.55	3.08		29.2	5.7	3.0	
Pd(Se$_2$CNEt$_2$)$_2$	red	290 (dec)	20.35	3.38			20.5	3.6		
Pd(Se$_2$CN(*i*-Bu)$_2$)$_2$	red	199–202	30.76	5.17			31.0	5.3		
Pd(Se$_2$CNEt$_2$)PPh$_3$Cl	red-orange	199–201	42.75	3.90			43.1	4.1		
Pd(Se$_2$CN(*i*-Bu)$_2$)PPh$_3$Cl	red-orange	228–230	46.18	4.74			46.0	4.8		
Pt(Se$_2$CNEt$_2$)$_2$	yellow	300 (dec)	17.68	2.94	4.12		17.5	3.1	4.1	
Pt(Se$_2$CN(*i*-Bu)$_2$)$_2$	yellow	216–218	27.32	4.58	3.40	39.91	27.4	4.7	3.6	39.8
Pt(Se$_2$CNEt$_2$)PPh$_3$Cl	yellow	205–208	37.59	3.43			37.6	3.3		
Pt(Se$_2$CN(*i*-Bu)$_2$)PPh$_3$Cl	yellow	237–240	41.00	4.21	1.77		40.8	4.2	1.8	
Pt(Se$_2$CNEt$_2$)PPh$_3$CH$_3$	yellow	167–169	40.34	3.95		22.10	40.3	4.1		21.9
Pt(Se$_2$CN(*i*-Bu)$_2$)(PPh$_3$)$_2$Cl	white	224 (dec)	51.31	4.60	1.33		51.3	5.8	1.1	
cis-Pt(Se$_2$CN(*i*-Bu)$_2$)$_2$Br$_2$	red-orange	233–236	22.73	3.81			22.9	3.8		
cis-Pt(Se$_2$CN(*i*-Bu)$_2$)$_2$I$_2$	dark red	178–182	20.67	3.47			20.8	3.6		
[Pt(Se$_2$CN(*i*-Bu)$_2$)$_3$]Cl	orange	298–300	28.83	4.84	3.74		28.9	5.2	3.7	
Pt(Se$_2$CNEt$_2$)PPh$_3$I	yellow	193–195	33.43	3.05	1.70		33.6	3.0	1.8	
Pd(Se$_2$CNEt$_2$)PEt$_3$Cl	orange-red	202–205	26.32	5.02	2.79		26.7	5.2	2.8	
Co(Se$_2$CNEt$_2$)$_3$	dark brown	290–292	22.95	3.83	5.35		23.1	4.0	5.4	

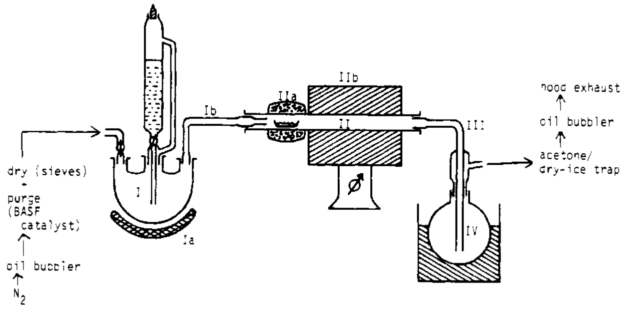

Figure 1. Apparatus for the preparation of CSe$_2$. I: methylene chloride vapor generator, 250-mL three-neck flask with gas inlet, a funnel containing CH$_2$Cl$_2$ with a pressure-equalizing arm and a connecting tube (Ib). (Ia is a 250-mL heating mantle.) II: 62 × 3 cm Pyrex tube. (Section IIa (ca. 15 cm long) is wound with nichrome and is insulated all around by packing with asbestos pulp. The tube is mounted on a multiple unit furnace (IIb).) III: vacuum connector adapter with one end extended as shown. IV: 250-mL or 500-mL round-bottom flask placed in a dry ice/acetone bath.

in tube II, as shown. Purified nitrogen gas (ca. 30–50 bubbles/s) is then passed through the system. Flask I is heated up to between 150 and 200°, section IIa of the tube to 375–400°, and section IIb of the tube to 575°. As soon as regions IIa and IIb reach a temperature of about 300 and 525°, respectively, methylene chloride is allowed to drop into I at a rate of about 1 drop/s. Gradually, droplets of the greenish yellow liquid CSe$_2$ form on the walls of the connector adaptor (III). A copious amount is formed as the temperatures in regions IIa and IIb reach 375 and 575°, respectively. As the reaction proceeds, a white mist is observed in the receiver flask (IV). If the mist is a reddish color, indicating that some Se is unreacted, the temperature of IIa is lowered. If IIb is raised much above 575°, decomposition of CSe$_2$ results and black carbon deposits start to form in the connector tube (III) and receiving flask (IV). The reaction usually is complete in 2–3 h.

Flask IV is taken off, quickly stoppered, and taken into a glovebox located in a fume hood. (*CSe$_2$ has been classified as highly toxic.*[3] *It has a very unpleasant odor even at low concentration. Extreme care must be taken in handling the compound.*) Another flask is placed in position IV. The glovebox (a simple Lucite box) is connected to a nitrogen source and through a liquid-nitrogen trap to the vacuum line. Any CSe$_2$ collected in the trap is later destroyed by adding saturated NaOH solution. The liquid obtained is usually contaminated with black and red solids. It is filtered through neutral alumina. The clear greenish yellow liquid thus obtained is a solution of CSe$_2$ in unreacted CH$_2$Cl$_2$.

For our purposes, it is not necessary to remove the CH$_2$Cl$_2$. Rosenbaum et al.[19] have published a plot of the density of a mixture of CSe$_2$/CH$_2$Cl$_2$ vs. the weight percent of CSe$_2$ in the mixture. On the basis of these data, a rough content of CSe$_2$ in the solution can be obtained and usually calculates to a yield of greater than 80% on the basis of Se. In this form, in a closed container, the CSe$_2$ can be stored at dry-ice temperature (–78 °C) for 2–3 months with little, if any, decomposition.

Dialkyldiselenocarbamate Salts. The preparation of both the potassium and dialkylammonium salts reported by Rosenbaum et al.[19] is closely followed.

Metal Complexes, M(Se$_2$CNR$_2$)$_2$. The preparation of complexes of this type has been previously reported.[7]

Chloro(*N*,*N*-diethyldiselenocarbamato)(triethylphosphine)nickel(II), Ni(Se$_2$CNEt$_2$)PEt$_3$Cl. Ni(Se$_2$CNEt$_2$)$_2$ (0.54 g) was suspended in 75 mL of acetone. Ni(PEt$_3$)$_2$Cl$_2$ (0.37 g) was dissolved in 25 mL of acetone. While the Ni(Se$_2$CNEt$_2$)$_2$ suspension was stirred, the Ni(PEt$_3$)$_2$Cl$_2$ solution was added. The suspension slowly turned deep red. After the suspension was stirred for 30 min, a dark red solution formed. Stirring was stopped, and 60 mL of petroleum ether was added, and the solution was left standing in the hood for crystallization. When the volume evaporated down to about 50 mL, more petroleum ether (100 mL) was added. The solution was stored in the freezer for several hours. Very dark red crystals formed, and these were washed with petroleum ether and dried under vacuum: yield, 0.75 g (82%); mp 92–95 °C (at 80 °C the color started to turn darker, at 90 °C it was almost black, and at 92 °C it started to melt, giving a dark red liquid).

Chloro(*N*,*N*-diethyldiselenocarbamato)(triphenylphosphine)palladium(II), Pd(Se$_2$CNEt$_2$)PPh$_3$Cl. Pd(Se$_2$CNEt$_2$)$_2$ (0.79 g) and Pd(PPh$_3$)$_2$Cl$_2$ (0.94 g) were mixed in 30–50 mL of benzene (refluxed over sodium benzophenone before use). Under argon, the suspension was stirred and heated at reflux. After being heated for about 15 min, the suspension cleared up to give an orange red solution. Heating was stopped after 3 h. The solution was filtered while still warm. Upon cooling, crystals formed. Addition of petroleum ether and cooling in the freezer yielded more crystals. The crystals were filtered off, washed with petroleum ether once, and dried under vacuum. The crystals were then recrystallized from CHCl$_3$/heptane. The yield was 0.7 g (60%). The diisobutyldiselenocarbamate analogue was prepared in a similar manner.

Chloro(*N*,*N*-diethyldiselenocarbamato)(triphenylphosphine)platinum(II), Pt(Se$_2$CNEt$_2$)PPh$_3$Cl. Pt(Se$_2$CNEt$_2$)$_2$ (0.58 g) and Pt(PPh$_3$)$_2$Cl$_2$ (0.66g) were mixed in 35 mL of benzene (refluxed over sodium benzophenone before use). The mixture was refluxed under nitrogen for about 7 h at the end of which the mixture had cleared to a yellow solution. No yellow precipitate (indicating unreacted Pt(Se$_2$CNEt$_2$)$_2$) was formed on cooling. The yellow solution was filtered and the filtrate evaporated to dryness. The yellow solid was

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[19] Rosenbaum, V. A.; Kirchberg, H.; Leibnitz, E. *J. Prakt. Chem.* **1963**, *19*, 1.

Table II. ^1H NMR Parameters of Diselenocarbamates

compd	solvent	δ[a]			*J*, Hz		
		CH_3	CH_2	CH	CH_3-CH	CH_2-CH	CH_3-CH_2
$K(Se_2CN(i\text{-}Bu)_2)$	acetone-d_6	0.90	4.12	2.68	6.5	7.0	
$CH_2(Se_2CN(i\text{-}Bu)_2)_2$	$CDCl_3$	0.95	3.55	2.48	6.5	7.0	
			4.01			7.5	
			5.45[b]				
$Zn(Se_2CNEt_2)_2$	$CDCl_3$	1.35	3.79				7.0
$Zn(Se_2CN(i\text{-}Bu)_2)_2$	$CDCl_3$	1.00	3.73	2.48	6.5	7.5	
$(NH_2Et_2)Se_2CNEt_2$	$CDCl_3$	1.27	3.23				7.0
		1.42	4.10				7.5
$Ni(Se_2CNEt_2)_2$	$CDCl_3$	1.28	3.66				7.0
$Ni(Se_2CN(i\text{-}Bu)_2)$	$CDCl_3$	0.94	3.50	2.28	6.5	7.5	
$Ni(Se_2CNEt_2)PEt_3Cl$[c]	$CDCl_3$	1.28	3.84				7.0
$Ni(Se_2CNEt_2)PMePh_2Cl$[f]	$CDCl_3$	1.18	3.54				7.2
$Pd(Se_2CN(i\text{-}Bu)_2)_2$	$CDCl_3$	0.97	3.63	2.35	6.2	7.5	
$Pd(Se_2CNEt_2)PEt_3Cl$	$CDCl_3$	buried under	3.78				7.0
		PEt_3 multiplet	3.82				
$Pd(Se_2CNEt_2)PPh_3Cl$	$CDCl_3$	1.18	3.58				7.0
		1.26	3.76				7.0
$Pd(Se_2CNEt_2)_2$[e]	$CDCl_3$	1.32	3.76				
$Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$	$CDCl_3$	0.87	3.43	2.22	6.0	7.5	
		0.93	3.58		6.0	7.5	
$Pt(Se_2CNEt_2)_2$	$CDCl_3$	1.34	3.61				7.2
$Pt(Se_2CN(i\text{-}Bu)_2)_2$	$CDCl_3$	0.98	3.46	2.36	6.2	7.5	
$Pt(Se_2CNEt_2)PPh_3Cl$	$CDCl_3$	1.19	3.49				7.0
		1.28	3.67				7.5
$Pt(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$	$CDCl_3$	0.88	3.31	2.25	6.5	7.0	
		0.94	3.50		6.5	7.0	
$Pt(Se_2CNEt_2)PPh_3CH_3$[d]	$CDCl_3$	1.23	3.63				7.0
		1.33	3.71				7.0
$Pt(Se_2CNEt_2)PPh_3I$	$CDCl_3$	1.21	3.43				7.0
		1.29	3.61				7.0
$[Pt(Se_2CN(i\text{-}Bu)_2)(PPh_3)_2]Cl$	$CDCl_3$	0.93	3.46	2.19	6.5	7.5	
$[Pt(Se_2CN(i\text{-}Bu)_2)_3]Cl$	$CDCl_3$	1.0	3.42	2.43	6.5	7.5	
cis-$Pt(Se_2CN(i\text{-}Bu)_2)_2I_2$	$CDCl_3$	0.97	3.17	2.17	6.0		
			3.28				
cis-$Pt(Se_2CN(i\text{-}Bu)_2)_2Br_2$	$CDCl_3$	1.0	3.33	2.3	6.5	7.5	
			3.40				
$Co(Se_2CNEt_2)_3$	$CDCl_3$	1.27	3.66				7.0
			3.71				7.5

[a] Downfield from Me_4Si. [b] CH_2 singlet, flanked by ^{77}Se satellites, $^2J_{Se-H} = 18$ Hz. [c] The triethylphosphine shows as a multiplet at 1.48 ppm. [d] The methyl peak falls at 0.57 ppm showing the following coupling constants: $^2J_{Pt-H} = 74$ Hz, $^3J_{P-H} = 4.5$ Hz, $^3J_{Xe-H} = 8.0$ Hz. [e] See ref 14. [f] $\delta(PCH_3Ph_2) = 1.95$ ppm; $^2J_{P-H} = 10.5$ Hz.

recrystallized from $CHCl_3$/acetone/heptane. The yield was 1.0 g (81%). The diisobutyldiselenocarbamate analogue was prepared in a similar manner.

Iodo(*N*,*N*-diethyldiselenocarbamato)(triphenylphosphine)platinum(II), $Pt(Se_2CNEt_2)PPh_3I$. $Pt(Se_2CNEt_2)PPh_3Cl$ (0.27 g) and NaI (0.09 g) were mixed in 25 mL of acetone and stirred for ca. 3 h. The mixture was filtered, leaving some white solid. The yellow filtrate was evaporated to give yellow crystals. These crystals were collected, washed with petroleum ether and air-dried. The yield was 0.24 g (77%).

Methyl(*N*,*N*-diethyldiselenocarbamato)(triphenylphosphine)platinum(II), $Pt(Se_2CNEt_2)PPh_3CH_3$. $Pt(Se_2CNEt_2)_2$ (0.18 g) and $Pt(PPH_3)_2(CH_3)_2$ (0.20 g) were mixed in 30 mL of benzene (refluxed over sodium benzophenone before use). Under argon, the mixture was stirred and heated at reflux. Heating was stopped after ca. 24 h. No precipitate formed, a good indication that the reaction was complete since both starting materials are only slightly soluble in benzene at room temperature. The clear solution was reduced in volume to ca. 10 mL. Some petroleum ether, 30–60° boiling range, was added until a light yellow precipitate began to form. The yellow product was recrystallized from $CHCl_3$/heptane. The yield was 0.21 g (55%).

Tris(*N*,*N*-diethyldiselenocarbamato)cobalt(III), $Co(Se_2CNEt_2)_3$. To an aqueous solution of 1 g of $CoCl_2·6H_2O$ in 30 mL of H_2O was added an ethanolic suspension of $(NEt_2H_2)Se_2CNEt_2$, 4 g in 30 mL of 95% ethanol, with vigorous stirring. A dark brown precipitate formed which was filtered off, washed with water, and recrystallized from $CHCl_3$.

Methylenebis(*N*,*N*-diisobutyldiselenocarbamate), $CH_2(Se_2CN(i\text{-}Bu)_2)_2$. This compound was obtained as a byproduct of an attempted preparation of $Pt(Se_2CN(i\text{-}Bu)_2)_2$ from $(N(i\text{-}Bu)_2H_2)Se_2CN(i\text{-}Bu)_2$ and K_2PtCl_4 in ethanol. The solid mass which resulted was dissolved in CH_2Cl_2 in an attempt to crystallize out a pure compound. Instead, the oxidized platinum complex $[Pt(Se_2CN(i\text{-}Bu)_2)_3]Cl$ and $CH_2(Se_2CN(i\text{-}Bu)_2)_2$ were isolated. The latter also could be prepared by the reaction of $Pt(Se_2CN(i\text{-}Bu)_2)_2$ with PPh_3 in CH_2Cl_2.

(*N*,*N*-Diisobutyldiselenocarbamato)bis(triphenylphosphine)platinum(II) Chloride, $[Pt(Se_2CN(i\text{-}Bu)_2)(PPh_3)_2]Cl$. Triphenylphosphine (0.5 g) and $Pt(Se_2CN(i\text{-}Bu)_2)_2$ (0.51 g) were placed in a Schlenk flask and evacuated. CH_2Cl_2 was vapor transferred into the flask. The solution was stirred for ca. 6 h in which time it turned from orange to light yellow. The solvent was partly stripped, and then diethyl ether was added until a white precipitate began to form. More white precipitate formed upon cooling. The flask was opened, and the white precipitate was filtered off and washed several times with ether. It was recrystallized from CH_2Cl_2/Et_2O. The yield was 0.65 g (90%). The filtrant was light yellow in color, containing $CH_2(Se_2CN(i\text{-}Bu_2)_2$ which was not isolated. The above reaction was also carried out in the presence of air. The same product was obtained.

***cis*-Dihalobis(*N*,*N*-diisobutyldiselenocarbamato)platinum(IV), *cis*-$Pt(Se_2CN(i\text{-}Bu)_2)_2X_2$ (X = I, Br).** These complexes were prepared according to the method used to prepared the dithio analogue as reported by Willemse et al.[20]

Physical Measurements. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are reported uncorrected. ^1H NMR spectra were observed on a Varian A 60A spectrometer (Table II). ^1H-decoupled ^{13}C (Table III) and ^{31}P (Table IV) NMR spectra were recorded on a Varian XL-100-15 spectrometer equipped

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(20) Willemse, J.; Cras, J. A.; Wijnhoven, J. G.; Beurskens, P. T. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 1199.

Table III. ^{13}C NMR Results for Diselenocarbamates

			δ			
compd	solvent	temp, °C	CH_2 (J_{C-P}, Hz)	CH	CH_3	phosphine[a] (J_{C-P}, Hz)
$Ni(Se_2CN(i\text{-}Bu)_2)_2$	$CDCl_3$	30	59.03	26.85	20.05	
$Ni(Se_2CNEt_2)PEt_3Cl$	$CDCl_3$	−40	47.49 46.31		12.47	12.85 (30.9), 8.12
$Pd(Se_2CN(i\text{-}Bu)_2)_2$	$CDCl_3$	30	59.79	26.98	20.12	
$Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$	$CDCl_3$	30	60.08	26.93	20.04	134.47 (11.2), 130.61 (2.0), 130.4 (44.2), 128.48 (10.0)
$Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$	$CDCl_3$	70	60.28	27.05	20.08 20.16	134.62 (11.3), 130.57 (2.2), 128.48 (10.0)
$Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$	$CDCl_3$	−30	59.72	26.68	19.95	134.24 (12.0), 130.66 (2.0), 128.48 (10.3)
$Pd(Se_2CNEt_2)PPh_3Cl$	$CDCl_3$	30	47.56 (br)[b] 47.41		12.53 12.28	134.48 (11.2), 130.28 (45.0), 130.66 (0.0), 128.50 (10.4)
$Pd(Se_2CNEt_2)PEt_3Cl$	$CDCl_3$	30	47.99 47.03 (1.9)		12.56 12.30	15.25 (26.2), 8.23 (1.8)
$Pd(Se_2CNEt_2)PEt_3Cl$	$CDCl_3$	70	48.07 47.10 (1.9)		12.59 12.32	15.63 (25.8), 8.29 (1.8)
$Pd(Se_2CNEt_2)PEt_3Cl$	$CDCl_3$	−30	47.90 46.87 (br) (~1.2[e])		12.53 12.29	14.56 (26.5), 8.14 (1.8)
$Pd(Se_2CNEt_2)PEt_3Cl$	C_6D_6	30	47.76 47.08 (br)		12.46 12.18	15.68 (26.2), 8.38 (0.0)
		90	47.91 47.23 (br)		12.47 12.22	16.34 (25.6), 8.48 (0.0)
$Pt(Se_2CN(i\text{-}Bu)_2)_2$	$CDCl_3$	30	59.16	26.81	20.06	
$Pt(Se_2CN(i\text{-}Bu)_2)(PPh_3)_2Cl$	$CDCl_3$	30	60.25	27.05	20.02	134.18 (t), 131.89 (s), 128.69 (t)[c]
cis-$Pt(Se_2CN(i\text{-}Bu)_2)_2I_2$	$CDCl_3$	14	59.19 58.59	27.07 26.89	20.32	
cis-$Pt(Se_2CN(i\text{-}Bu)_2)_2I_2$	$CDCl_3$	47	59.46 58.81	27.19 27.02	20.40	
$Pt(Se_2CNEt_2)PPh_3Cl$	$CDCl_3$	30	47.57 (br) 47.39		12.47 12.22	134.35 (10.4) (J_{C-Pt} = 21.6 Hz), 130.72 (2.3) 129.90 (56.3), 128.28 (10.6)
$Pt(Se_2CNEt_2)PPh_3Cl$	$CDCl_3$	−40	47.30 47.22 (br)		12.48 12.17	134.04 (10.5) (J_{C-Pt} = 21.0 Hz), 130.79 (0.0) 128.30 (10.8)
$Pt(Se_2CNEt_2)PPh_3CH_3$	$CDCl_3$	30	47.77 (br) 46.42		12.23 −13.09 ($^2J_{C-P}$ = 7.2 Hz; $^1J_{C-Pt}$ = 621.5 Hz)[d]	133.98 (11.3) ($^3J_{C-Pt}$ = 29.0 Hz), 131.72 (55.0) 130.08 (2.5), 128.07 (11.1)
$Pt(Se_2CNEt_2)PPh_3CH_3$	$CDCl_3$	−40	47.76 (br) 46.21		12.18 −13.18 ($^2J_{C-P}$ = 7.3 Hz)	133.76 (11.3) ($^3J_{C-Pt}$ = 29.0 Hz), 131.04 (56.0) 130.16 (1.5), 128.09 (10.5)
$Pt(Se_2CNEt_2)PPh_3CH_3$	C_6D_6	90	47.68 (2.4) 46.43		12.19	134.65 (11.3), 130.15 (2.3), 128.31 (10.3)

[a] In the triphenylphosphine, the carbon bonded to P is sometimes not observed due to saturation. [b] br = broad. [c] t = triplet; s = singlet. [d] Methyl group coordinated to Pt. [e] Uncertain due to broadening.

Table IV. Selected ^{31}P NMR Spectral Results for the Diselenocarbamates

compd	δ[a]	J_{P-Pt}, Hz	J_{P-Se},[b] Hz
$Pt(Se_2CNEt_2)PPh_3CH_3$	21.1	4067.3	112.1
$Pt(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$	13.2	3620.2	100.2
$[Pt(Se_2CN(i\text{-}Bu)_2)(PPh_3)_2]Cl$	15.9	3235.0	complex
$Pd(Se_2CNEt_2)PPh_3Cl$	27.1		103.9
$Ni(Se_2CNEt_2)PEt_3Cl$	16.1		51; 25 (br satellites)
PEt_3	−12.25		
PPh_3	−4.4		

[a] All spectra obtained from $CDCl_3$ solutions at ambient temperature; (external) reference is 85% H_3PO_4; downfield shift is positive. [b] Only ^{31}P–^{77}Se couplings to ^{77}Se trans to ^{31}P are reported, except for $Ni(Se_2CNEt_2)PEt_3Cl$. Cis couplings are generally less than 10 Hz.

Table V. Crystallographic Data for $Pt(Se_2CN(i\text{-}Bu)_2)_2$

molecular formula	$PtC_{18}N_2Se_4H_{36}$
fw	791.43
cell const (22 °C)	
a, Å	6.736 (1)
b, Å	12.357 (2)
c, Å	15.496 (4)
β, deg	99.03 (2)
vol, Å^3	1273.97 (32)
d_{calcd}, g cm^{-3}	2.06
d_{obsd}, g cm^{-3} (by floatation)	2.03
Z, formula units per cell	2
λ(Mo Kα), Å	0.710 73
cryst dimens, mm^3	0.2 × 0.2 × 0.3
linear absorption, cm^{-1}	119.2
systematic abs	$h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$
space group	C_{2h}^5, $P2_1/c$ (No. 14)
2θ limits, deg	2.0–55.0
unique data, $I = 3\sigma_I$	1527
no. variables	115
R/R_w (statistical weights)	0.068/0.074

with Fourier transform and Gyro observe capabilities and operating at 25.16 and 40.54 MHz, respectively (Table IV). A Varian V6040 temperature controller was used in the variable-temperature studies. On the XL-100, low temperatures were measured by using a calibrated SGA Scientific Inc. JM-7600 thermometer insereted in a tube containing the appropriate solvent. Field-frequency lock was effected by using deuterated solvents (Norell). ^{1}H and ^{13}C chemical shifts are reported relative to tetramethylsilane while ^{31}P chemical shifts were compared with external 85% phosphoric acid. Chemical shifts downfield of the reference are indicated positive.

Crystallographic Measurements. A suitable crystal of $Pt(Se_2CN(i\text{-}Bu)_2)_2$ was mounted parallel to its long axis on a glass fiber. After centering and indexing, data were obtained on a Syntex P2$_1$ automatic diffractometer (Table V). The structure was solved by heavy-atom (Patterson) technique and refined to an isotropic convergence for the 13 nonhydrogen atoms. The programs used and general computational

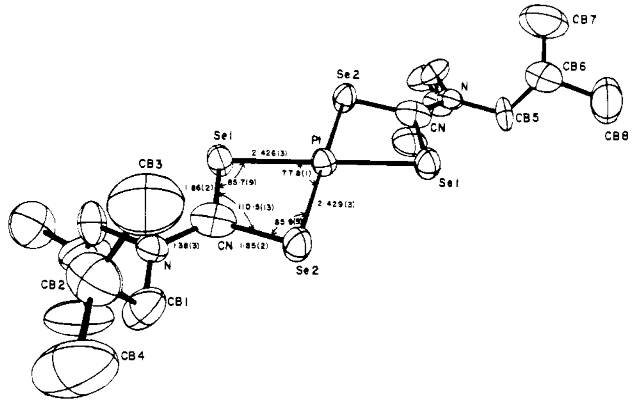

Figure 2. Structure and selected dimensions of $Pt(Se_2CN(i\text{-}Bu)_2)_2$.

Table VI. Positional Parameters and Estimated Standard Deviations of $Pt(Se_2CN(i\text{-}Bu)_2)_2$

	x	y	z
Pt	0.0000	0.5000	0.5000
Se1	0.1708 (3)	0.5989 (2)	0.6252 (2)
Se2	−0.2774 (3)	0.5882 (2)	0.5549 (2)
N	−0.1141 (28)	0.7282 (14)	0.6980 (11)
CN	−0.0824 (34)	0.6510 (19)	0.6370 (15)
CB1	−0.3175 (33)	0.7718 (18)	0.6977 (16)
CB2	−0.3242 (39)	0.8945 (19)	0.6641 (16)
CB3	−0.2773 (48)	0.9022 (25)	0.5747 (20)
CB4	−0.5342 (38)	0.9352 (23)	0.6677 (22)
CB5	0.0564 (34)	0.7688 (18)	0.7602 (13)
CB6	0.1096 (45)	0.6983 (28)	0.8411 (18)
CB7	−0.0418 (46)	0.6751 (35)	0.8893 (21)
CB8	0.2973 (44)	0.7465 (28)	0.8979 (18)

procedures have been described.[37] Absorption corrections were not deemed to be cost effective since the crystal was reasonably symmetric. Table VI lists potential parameters. Figure 2 presents an ORTEP drawing of the structure which includes selected bond lengths and angles. Additional information includes thermal parameters (Table VII) and structure factors (see Appendix).

Results

Preparation of Compounds. Using the present method to prepare CSe_2, we have been able to achieve yields greater than 80% routinely. With care, speed, and working in the hood (equipped with a good exhaust) at all times, we have managed to keep the CSe_2 vapor from the laboratory area. As obtained, CSe_2 is in CH_2Cl_2, and it can be used directly for the preparation of the dialkylammonium dialkyldiselenocarbamates. These salts are generally prepared by the slow addition of the CSe_2 solution to an excess of the dialkylamine in petroleum ether (ca. five times the volume of the CSe_2 solution at 0 °C and under nitrogen. When diethylamine is used, the yellow diethylammonium salt precipitates immediately. However, when diisobutylamine is used, the diisobutylammonium salt remains in solution. In this case, the solution is first concentrated to about half the initial volume and then cooled in dry ice overnight. The yellow dialkylammonium salt obtained is filtered and generously washed with petroleum ether until it no longer smells of the amine. The filtration and washings are carried out in air.

The dialkylammonium diselenocarbamates are not indefinitely stable in air. The diisobutylammonium salt decompose within days is kept at room temperature. The diethylammonium salt can be kept longer at room temperature if kept dry. In order to avoid decomposition, the dialkyldiselenocarbamates are usually stored as the zinc complex. The zinc can be readily displaced by other metals such as those reported here.

The method used to prepare the complexes $M(Se_2CNR_2)PR'_3X$ (M = Ni, Pd, Pt; R = Et, *i*-Bu; R′ = Et, Ph; X = Cl, I, CH_3) is a new one. Attempts to prepare these complexes with the method used to prepare the dithio analogue[6] were not very successful. The present approach is simple, gives high yields, and shows no evidence of interferring side products. This new method also works well for the preparation of the dithio analogues.

The structure of $Pt(Se_2CN(i\text{-}Bu)_2)_2$ supports the contention[11] that replacement of S by Se leads to few significant changes. There is a slight 4.5° twist away from planarity of the Se1, Se2, CN plane from the N, CBl, CB5 plane for this centric molecule, but this twist may be caused by asymmetric packing of the isobutyl groups. The N–CN distance of 1.38 (3) Å is slightly larger (~0.02–0.07 Å) than the distance generally found in dithiocarbamates but within three standard deviations of the length reported for nearly all other structures of dithio- or diselenocarbamates. Some intramolecular distances and angles are reported in Table VIII.

NMR Results. The ^1H results are presented in Table II. Some results have been reported by other previously[12] (those of $M(Se_2CNEt_2)_2$; M = Ni, Pd, Pt) and are included in Table II for comparison. In general, for the complexes of the type $M(Se_2CNR_2)_2$ where R is ethyl, the methylene quartet falls in the region of 3.5 ppm while the methyl triplet falls at around 1.3 ppm. When R is isobutyl, the methylene doublet falls around 3.5 ppm followed by the methine multiplet at about 2.3 ppm and the methyl doublet at around 0.95 ppm. The observed ^1H–^1H coupling constants are normal for three-bond couplings.

In the complexes, $M(Se_2CNR_2)PR_3'X$, the alkyl groups are nonequivalent at the probe temperature (ca. 36 °C) except for the Ni complex. For the Pd and Pt complexes when X = Cl or I and R = Et, the nonequivalent methylene and methyl peaks are generally separated by about 0.18 and 0.08 ppm, respectively. However, in $Pt(Se_2CNEt_2)PPh_3Me$, the methylene peaks are separated by 0.08 ppm and the methyl peaks by 0.10 ppm. The $^2J_{H-Pt}$ of 74 Hz is similar to the observed values in *trans*- and *cis*-$PtMeXL_2$ (X = halide) and $PtMe_2L_2$ (L = phosphine) (50–90 Hz),[21] while the small $^3J_{H-P}$ of 4.5

Table VII. Thermal Parameters[a] and Estimated Standard Deviations for $Pt(Se_2CN(i\text{-}Bu)_2)_2$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.02307 (3)	0.0052 (2)	0.0033 (2)	−0.0000 (2)	0.0018 (2)	−0.00007 (2)
Se1	0.0193 (6)	0.0076 (2)	0.0037 (2)	0.0007 (3)	0.0010 (2)	−0.0016 (2)
Se2	0.0178 (7)	0.0071 (2)	0.0049 (2)	−0.0002 (3)	0.0015 (2)	−0.0022 (2)
N	0.0254 (57)	0.0054 (15)	0.0033 (10)	−0.0018 (25)	0.0044 (19)	−0.0002 (10)
CN	0.0272 (71)	0.0074 (21)	0.0051 (13)	0.0056 (33)	0.0030 (26)	0.0033 (14)
CB1	0.0202 (65)	0.0056 (19)	0.0072 (16)	−0.0005 (30)	0.0022 (26)	−0.0001 (14)
CB2	0.0391 (88)	0.0061 (20)	0.0058 (15)	0.0037 (36)	0.0053 (30)	0.0010 (14)
CB3	0.052 (12)	0.0122 (29)	0.0078 (19)	0.0009 (52)	0.0041 (39)	0.0040 (20)
CB4	0.0251 (79)	0.0097 (25)	0.0140 (26)	0.0054 (39)	0.0078 (38)	0.0013 (21)
CB5	0.0302 (80)	0.0081 (22)	0.0025 (11)	−0.0006 (35)	−0.0029 (25)	−0.0014 (13)
CB6	0.040 (10)	0.0182 (37)	0.0054 (16)	−0.0066 (55)	0.0027 (35)	0.0025 (21)
CB7	0.038 (11)	0.0267 (53)	0.0086 (22)	0.0023 (64)	0.0080 (40)	0.0057 (28)
CN8	0.0392 (98)	0.0189 (39)	0.0055 (16)	−0.0004 (54)	−0.0036 (34)	−0.0017 (20)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table VIII. Intramolecular Distances and Bond Angles and Their Estimated Standard Deviations for $Pt(Se_2CN(i\text{-}Bu)_2)_2$

Bonded Distances, Å			
Pt-Se1	2.426 (3)	CB1-CB2	1.60 (3)
Pt-Se2	2.429 (3)	CB2-CB3	1.47 (4)
CN-Se1	1.86 (2)	CB2-CB4	1.51 (4)
CN-Se2	1.85 (2)	CB5-CB6	1.52 (4)
CN-N	1.38 (3)	CB6-CB7	1.38 (5)
N-CB1	1.47 (3)	CB6-CB8	1.54 (4)
N-CB5	1.47 (3)		
Nonbonded Distances, Å			
Se1---Se2	3.048 (3)	Se1---CB5	3.14 (2)
Pt---CN	2.94 (2)	Se2---CB1	3.21 (2)
Bond Angles, Deg			
Se1-Pt-Se2	77.8 (1)	CB1-CB2-CB3	111.6 (19)
Pt-Se1-CN	85.7 (9)	CB1-CB2-CB4	106.3 (18)
Pt-Se2-CN	85.8 (9)	CB3-CB2-CB4	110.8 (20)
Se1-CN-Se2	110.5 (13)	CB1-N-CB5	120.6 (15)
Se1-CN-N	123.3 (15)	N-CB5-CB6	113.8 (17)
Se2-CN-N	126.2 (16)	CB5-CB6-CB7	117.7 (23)
CN-N-CB1	119.6 (15)	CB5-CB6-CB8	108.4 (21)
CN-N-CB5	119.7 (15)	CB7-CB6-CB8	112.2 (23)
N-CB1-CB2	109.1 (16)		

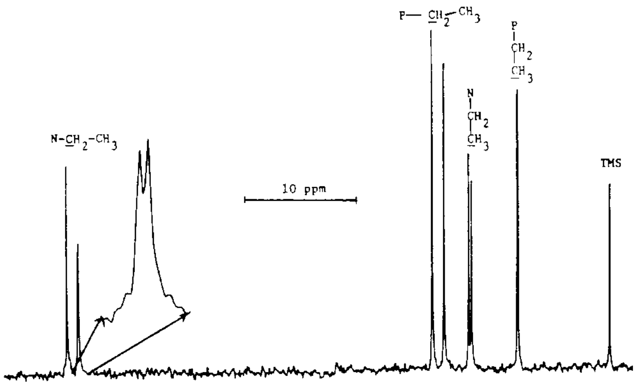

Figure 3. ^{13}C (^1H) NMR spectrum of $Pd(Se_2CNEt_2)PEt_3$ in $CDCl_3$ at 30 °C.

Hz is expected for a methyl group being cis to a phosphine group. Ruddick and Shaw[22] previously reported $^3J_{H-P}$ to be about 4.5 and 7.0 Hz in each of the complexes *cis*-$PtMeXL_2$ ($X = Cl, N_3^-$; $L = PMePh_2, PMe_2Ph$). They could not be certain, however, which of the $^3J_{H-P}$'s in each complex arises from cis coupling and which from trans coupling.

No study of the ^{13}C NMR of diselenocarbamates has appeared previously. Table V consitutes the first such report. The ^{13}C chemical shifts reported are very similar to those reported for the dithiocarbamates.[23,24] In the present study, the ^{13}C signal of the CSe_2 moiety was not clearly observable. (Chemical shift information obtained from this carbon potentially could be useful as shown by Lin[25] who was able to observe this carbon signal in the dithiocarbamate analogue, 30% enriched with ^{13}C at CS_2.)

In the unsymmetrical complexes, $M(Se_2CNR_2)PR'_3X$, some of the results are notable. The ^1H NMR of $Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$ shows two sets of isobutyl proton resonances (see Table II) while, in the corresponding ^{13}C NMR, only one set of isobutyl carbon resonances are observed (Table III). When the isobutyl groups are replaced by ethyl groups, the methylene and methyl carbons show two sets of ^{13}C resonances (see Table III). In these cases, one of the methylene peaks is either broad or further split into a doublet; for example, see Figure 3. It is also noted that the $M(Se_2CNEt_2)PPh_3Cl$ (M = Pd, Pt) and $Pt(Se_2CNEt_2)PPh_3Me$, the broad methylene peak is downfield of the sharp methylene peak at room temperature while, in $Pd(Se_2CNEt_2)PEt_3Cl$, the methylene peak (at 47.0 ppm) that is split into a doublet is upfield of the singlet methylene peak (at 48.0 ppm) (Figure 3).

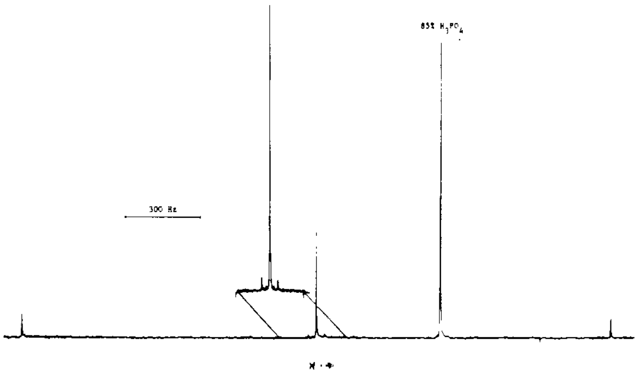

Figure 4. ^{31}P (^1H) NMR spectrum of $Pt(Se_2CNEt_2)PPh_3Me$ in $CDCl_3$ at 30 °C. The small peaks in the insert are ^{13}C satellites.

The ^{13}C NMR spectra of $Pd(Se_2CNEt_2)PPh_3Cl$ also were obtained with use of a higher frequency (45.3 MHz).[26] At this frequency, the methyl peak separation was found to be larger (11.1 Hz) than at 25.2 MHz (6.4 Hz). Similarly, the methlyene peak separation is 8.3 Hz at 45.3 MHz and 3.8 Hz at 25.2 MHz. These results show that the splittings are due to chemical shift differences and not to spin–spin coupling. A sample of $Pd(Se_2CNEt_2)PEt_3Cl$ also was run at 45.3 MHz to see the effect on the upfield methylene peaks at 47.0 ppm. The separation of the peaks is about 1.5 Hz. The separation of these peaks at 25.2 MHz is 1.9 Hz. Thus the splitting of the upfield methylene peak is due to spin–spin coupling. If the splitting were due to chemical shift differences, the separation expected at 45.3 MHz is 3.4 Hz.

When C_6D_6 is used as solvent, the upfield methylene resonance (47.0 ppm) of $Pd(Se_2CNEt_2)PEt_3Cl$ is no longer resolved into a doublet as in $CDCl_3$ but instead appears as a broad peak. An opposite behavior is observed in $Pt(Se_2CNEt_2)PPh_3Me$ where in $CDCl_3$, the upfield methylene carbon resonance is broad at 30 and −40 °C, but in C_6D_6, at 90 °C, this peak is split into a doublet.

In general, varying the temperature changes the observed chemical shifts by a small amount (less than 0.5 ppm). In $Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$, a splitting of 0.09 ppm of the methyl peak is seen at 70 °C. The upfield methylene doublet (47.0 ppm) of $Pd(Se_2CNEt_2)PEt_3Cl$ broadens at low temperatures, and at −30 °C the splitting could barely be observed. For the rest of the complexes, the ^{13}C NMR changes with temperature are quite unremarkable.

Only a few ^{31}P NMR results have been obtained, and these are reported in Table V. The ^{31}P chemical shifts for PEt_3 and PPh_3 have been included for comparison. Upon coordination, the phosphine resonance invariably shifts downfield.

In the Pt complexes, the ^{31}P–^{195}Pt coupling constants are as generally expected.[27,28] The $^1J_{P-Pt}$ in $Pt(Se_2CN(i\text{-}Bu)_2)(PPh_3)_2Cl$ is normal (~3000 Hz) for cis bis(phosphine) complexes (trans bis(phosphine) complexes usually have $^1J_{P-Pt}$ less than 3000 Hz). The relatively large $^1J_{P-Pt}$ in the Pt–Me complex is consistent with the published data[29] on *cis*-

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(21) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(22) Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2801.

(23) Lin, I. J. B.; Chen, H.-W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 394.

(24) Van Gall, H. L. M.; Diesveld, J. W.; Pijpers, F. W.; Van der Linden, J. G. M. *Inorg. Chem.* **1979**, *18*, 3251.

(25) Lin, I. J. B.. Ph.D. Thesis, Case Western Reserve University, 1975.

(26) The Brucker WP-180 NMR spectrometer was used for these measurements. The authors gratefully acknowledge Dr. Thomas Gerken for obtaining the ^{13}C spectra.

(27) Allen, F. H.; Sze, S. N. *J. Chem. Soc. A* **1971**, 2054.

(28) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

(29) Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700.

$PtMeX(PEt_3)_2$ in which $^1J_{P-Pt}$ of the phosphine cis to Me is about 4000 Hz. Figure 4 is a ^{31}P spectrum of $Pt(Se_2CNEt_2)PPh_3Me$ exhibiting the coupling to both ^{195}Pt and ^{77}Se.

No two-bond ^{31}P–^{77}Se coupling constants previously have been reported. (One-bond ^{31}P–^{77}Se couplings in $(CH_3)_2PSeCH_3$ and $(CH_3)_2P(S)SeCH_3$ have been reported[30] to be 205 and 341 Hz, respectively) Only the trans ^{31}P–^{77}Se coupling for the Pt and Pd complexes are reported here. The cis couplings are small[7] (10 Hz or less), and the resulting satellites are usually "fused" into the center peak (see, for example, Figure 4).

Discussion

Two reactions[1,5] have been used to prepare CSe_2 (eq 1 and 2). Reaction 1 involves using a known carcinogen, CCl_4, and

$$CCl_4 + 2H_2Se \rightarrow CSe_2 + 4HCl \qquad (1)$$

$$CH_2Cl_2 + 2Se \rightarrow CSe_2 + 2HCl \qquad (2)$$

H_2Se gas, the most toxic Se compound known, being toxic at a level of 0.2 mg of Se/m^3 of air.[4] Also, reaction 1 possesses no advantage in procedure and yield over reaction 2; hence we prefer the latter for laboratory syntheses.

The $Pt(Se_2CN(i\text{-}Bu)_2)_2$ structure (Figure 2) is typical[11] of the structure of nickel triad bis(dithiocarbamate) and bis(diselenocarbamate). The ligand including the first two carbon atoms of the alkyl groups is generally planar with a rather short C–N bond length. The slightly longer, ~0.05 Å, C–N "selenoureide" distance observed here may be significant although too few structure comparing S and Se derivatives have appeared to date to warrant discussion at this time. The Pt–Se distance is 0.11 Å longer than the Pt–S distance[1] in $Pt(S_2CNEt_2)_2$, a difference identical with the difference observed between the Ni–Se and Ni–S distances in the nickel analogues.

The syntheses and characterization of transition-metal complexes containing only *N,N*-dialkyldiselenocarbamates as ligands have been reported by, among others, Barnard and Woodbridge,[3] Rosenbaum et al.,[19] Furlani et al.,[31] and Jensen et al.[9] Complexes of the type $M(Se_2CNR_2)PR'_3Cl$ have not been previously reported, and the method of preparing them is different from that of the dithio analogues.[6,32] Tanaka and Sonoda[33] have prepared the thioselenocarbamato analogue $Pd(SeSCNR_2)PR'_3Cl$ by reacting $\{Pd(PR_3)Cl_2\}_2$ with $(CH_3)_2SnCl(SSeCNR_2)$.

The method used to prepare $Pt(Se_2CNEt_2)PPh_3CH_3$ is an extension of that used for preparing the chloride derivative, with $Pt(CH_3)_2(PPh_3)_2$ in place of $PtCl_2(PPh_3)_2$. The yield, while somewhat lower than that of the chloride derivatives, is slightly above 50%. This light yellow complex is stable in air. Its structure recently has been reported.[34]

Examination of Table II shows that ^1H NMR spectroscopy can give useful qualitative information about the diselenocarbamates. In particular, the chemical shift of the methylene protons, which are the nearest to the nitrogen, are sensitive to the metal as well as the other ligands on the metal. In general, the ^1H chemical shifts in the dithiocarbamates[12,32,35] are slightly upfield (by ca. 0.05 ppm) of those in the diselenocarbamates.

Various factors influence the ^1H chemical shifts in the diselenocarbamates, including contributions from delocalization of electron density in the Se_2CN portion of the ligand. No clear trends exist but it appears that the chemical shifts of the first carbon atom of the alkyl groups bound to N are sensitive to changes in the bonding at selenium.

In the unsymmetrical complexes, $M(Se_2CNR_2)PR'_3X$ (M = Pd, Pt), the phenyl group on the triphenylphosphine appears to make a significant contribution to the NCH_2 chemical shifts. A similar result has been suggested by Tanaka et al.[33] in their study of the Pd complex of the thioseleno analogues. The crystal structure of $Pt(Se_2CNEt_2)PPh_3Cl$[36] shows that one of the phenyl rings on the phosphine lies perpendicular to the $PtSe_2PCl$ plane of the molecule with the first carbon atom of the ring in the plane of the molecule. The center of this ring is about 6.5 Å away from the closer of the two NCH_2 carbon atoms. At 6.5-Å distance, the diamagnetic ring current effect can be calculated[37] to give a shift of about 0.12 ppm while, at 5.5 Å, a shift of about 0.25 ppm results. In each of the complexes, $M(Se_2CNR_2)PPh_3Cl$ (M = Pd, Pt; R = Et, *i*-Bu), the chemical shift differences between the two sets of NCH_2 protons range between 0.15 and 0.19 ppm. In $Pd(Se_2CNEt_2)PEt_3Cl$, however, the corresponding chemical shifts differ only by 0.04 ppm. Thus the ring current effect of the phosphine phenyl groups contribute to the chemical shift of the NCH_2 protons.

An extensive collection of ^{13}C NMR spectra of dithiocarbamate-containing complexes has recently been published by van der Linden et al.[24] Unfortunately the lack of correspondence of the alkyl groups on the dichalcogenocarbamates and other donor groups on the metals with those in the present study allows only a very limited comparison to be made between our results and van der Linden's. In general, the NCH_2 carbon resonances of the diseleno complexes are downfield of those of the dithio analogues by about 3 ppm. This may reflect a slightly greater positive charge on the N atom in the selenium analogues, a reasonable result of the decreased ability of Se compared with S to π bond to the adjacent C atom. Like the ^1H chemical shifts, the ^{13}C chemical shifts of the diselenocarbamates are sensitive to changes of the metal as well as the other ligands on the metal.

The observation of only one set of isobutyl ^{13}C resonances for $Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$ at ambient temperatures could be caused by an accidental degeneracy. Alternatively, chemical exchange could produce the effect. Since the ^1H NMR shows well-resolved nonequivalent isobutyl groups, an exchange rate would need to be intermediate between the ^1H and ^{13}C NMR time scales. However, the splitting of the methyl carbon peaks observed at 70 °C is not consistent with this explanation. Accidental degeneracy appears to be the more likely. The other two Pd complexes, $Pd(Se_2CNEt_2)PR_3Cl$ ($PR_3 = PPh_3$, PEt_3), show chemical shifts for the two sets of NCH_2 carbon resonances that are solvent and temperature variable. Hence under the right conditions, the resonances may become coincidental.

One of the NCH_2 resonances is broadened or split in $M(Se_2CNEt_2)PR_3X$ (M = Pd, Pt; R = Ph, Et; X = Cl, Me). ^1H, ^{77}Se,[7] and ^{31}P NMR indicate that the complexes do not dissociate appreciably in solution. The origin of this splitting appears to be a five-bond spin–spin coupling to ^{31}P, the only other nucleus with spin $^1/_2$ (other than ^1H which is decoupled) in the molecule.

Unlike the dithiocarbamate complexes, a special feature of the diselenocarbamate complexes is the observation of satellites in the ^{31}P NMR arising from spin–spin coupling to ^{77}Se. These

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(30) McFarlane, W.; Nash, J. A. *Chem. Commun.* **1969**, 913.

(31) Furlani, C.; Cervone, E.; Camassei, F. D. *Inorg. Chem.* **1968**, *7*, 265.

(32) Cornock, M. C.; Stephenson, T. A. *J. Chem. Soc. A* **1977**, *501.*

(33) Sonoda, N.; Tanaka, T. *Inorg. Chim. Acta* **1975**, *12*, 261.

(34) Chen, H.-W.; Fackler, J. P., Jr.; Masters, A. F.; Pan, W.-H. *Inorg. Chim. Acta* **1979**, *35*, L333.

(35) Cornock, M. C.; Stephenson, T. A. *J. Chem. Soc. A* **1977**, 683.

(36) Unpublished results.

(37) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(38) Fackler, J. P., Jr.; Masters, A. F. *Inorg. Chim. Acta* **1980**, *39*, 111–118.

(39) The $2p\pi$–$3p\pi$ overlap of C–S π bonding is larger than the $2p\pi$–$4p\pi$ overlap required for C–Se π bonding at the observed bond distances.

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satellites can be useful for probing dynamic processes involving the metal–selenium bonds.[8] Only satellites arising from trans ^{31}P–^{77}Se coupling are clearly observed in the Pd and Pt complexes. The cis coupling is too small (<10 Hz), and the satellite arising from these are in the base of the main peak.

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Registry No. $K(Se_2CN(i\text{-}Bu)_2)$, 67994-90-5; $CH_2(Se_2CN(i\text{-}Bu)_2)_2$, 76137-25-2; $Zn(Se_2CNEt_2)_2$, 19400-58-9; $Zn(Se_2CN(i\text{-}Bu)_2)_2$, 68011-63-2; $(NH_2Et_2)Se_2CNEt_2$, 30634-02-7; $Ni(Se_2CNEt_2)_2$, 19400-59-0; $Ni(Se_2CN(i\text{-}Bu)_2)$, 68025-77-4; $Ni(Se_2CNEt_2)PEt_3Cl$, 67994-91-6; $Ni(Se_2CNEt_2)PMePh_2Cl$, 76136-18-0; $Pd(Se_2CN(i\text{-}Bu)_2)_2$, 68011-58-5; $Pd(Se_2CNEt_2)PEt_3Cl$, 76136-19-1; $Pd(Se_2CNEt_2)PPh_3Cl$, 76136-20-4; $Pd(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$, 68025-79-6; $Pt(Se_2CNEt_2)_2$, 19400-65-8; $Pt(Se_2CN(i\text{-}Bu)_2)_2$, 68025-75-2; $Pt(Se_2CNEt_2)PPh_3Cl$, 68011-59-6; $Pt(Se_2CN(i\text{-}Bu)_2)PPh_3Cl$, 68252-96-0; $Pt(Se_2CNEt_2)PPh_3CH_3$, 76136-21-5; $Pt(Se_2CNEt_2)PPh_3I$, 76136-22-6; $[Pt(Se_2CN(i\text{-}Bu)_2)(PPh_3)_2]Cl$, 68025-78-5; $[Pt(Se_2CN(i\text{-}Bu)_2)_3]Cl$, 76136-23-7; *cis*-$Pt(Se_2CN(i\text{-}Bu)_2)_2I_2$, 68011-50-7; *cis*-$Pt(Se_2CN(i\text{-}Bu)_2)_2Br_2$, 68011-61-0; $Co(Se_2CNEt_2)_3$, 76136-24-8; $Pd(Se_2CNEt_2)_2$, 19400-60-3; $Ni(PEt_3)_2Cl_2$, 17523-24-9; $Pd(PPh_3)_2Cl_2$, 13965-03-2; $Pt(PPh_3)_2Cl_2$, 10199-34-5; $Pt(PPh_3)_2(CH_3)_2$, 17567-35-0; K_2PtCl_4, 10025-99-7; $(N(i\text{-}Bu)_2H_2)Se_2CN(i\text{-}Bu)_2$, 76137-27-4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Mercury-Bridged Cobaltacarborane Complexes Containing B–Hg–B Three-Center Bonds. Synthesis and Structure of μ,μ'-$[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$ and μ-$[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]HgCl$ ($R = H, CH_3$) and Related Compounds[1]

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Reactions of the *nido*-cobaltacarborane anions $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4^-$ and $[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4^-$ with $HgCl_2$ in tetrahydrofuran give initially the unstable adducts $[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4\cdot HgCl_2]^-$ ($R = H, CH_3$), which lose Cl^- to form the isolable HgCl-bridged complexes μ-$[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]HgCl$; the latter species undergo symmetrization to generate the bis(cobaltacarboranyl)mercury complexes μ,μ'-$[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$. In the cyclopentadienyl system ($R = H$), the formation of the μ,μ' complex is rapid, giving high yields within minutes; in contrast, the pentamethylcyclopentadienyl species reacts much more slowly, requiring days to form the μ,μ' complex in isolable quantity. Thus, the characterization of the mono(cobaltacarboranyl)mercury complex is readily achieved with the $C_5(CH_3)_5$-substituted cobaltacarborane. The structural characterization of the Hg-bridged complexes is based on pulse Fourier transform ^1H and ^{11}B NMR, IR, and mass spectra, and single-crystal X-ray diffraction studies of μ-$[[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4]HgCl$ and μ,μ'-$[(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4]_2Hg$. The mono(cobaltacarboranyl) complex crystallizes as a dimer with weak intermolecular Hg···Cl interactions. Crystal data for $HgCoClC_{14}B_3H_{25}$: mol wt 520.76, space group $P2_1/n$, $Z = 2$, $a = 9.634$ (2) Å, $b = 14.05$ (1) Å, $c = 13.862$ (7) Å, $\beta = 96.71$ (3)°, $V = 1863$ Å^3, $R = 0.044$ for 1607 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for $HgCo_2C_{18}B_6H_{30}$: mol wt 629.75, space group $P2_1/n$, $Z = 2$, $a = 8.456$ (8) Å, $b = 11.334$ (7) Å, $c = 11.77$ (1) Å, $\beta = 100.12$ (9)°, $V = 1110$ Å^3, $R = 0.081$ for 1441 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

A recent report[2] from these laboratories described the preparation of the mercury-bridged complexes μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$ (I), μ,μ'-$(B_5H_8)_2Hg$ (II), and some chemistry based on these species. In the proposed structures[2] of I and II, a mercury atom interacts with a B–B edge on the open face of the *nido*-carborane or -borane ligand, forming a two-electron, three-center B–Hg–B bond. The general principle of boron–metal–boron bridging in nido-boranes and -carboranes is well established;[3] in addition to I and II, there are several known complexes in which a metal (or nonmetal) atom participates in B–M–B bridge-bonding on *two* separate ligands.[4] However, previous examples of well-characterized B–Hg–B bridging are virtually nonexistent.[5]

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(1) Based in part on a Ph.D. dissertation, University of Virginia, 1980, by D.C.F.

(2) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886.

(3) (a) Greenwood, N. N.; Ward, I. M. *Chem. Soc. Rev.* **1974**, *3*, 231. (b) Wegner, P. A. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 12.

(4) (a) Tabereaux, A.; Grimes, R. N. *Inorg. Chem.* **1973**, *12*, 792. (b) Davison, A.; Traficante, D. D.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 2802. (c) Denton, D. L.; Clayton, W. R.; Mangion, M.; Shore, S. G.; Meyers, E. A. *Inorg. Chem.* **1976**, *15*, 541. (d) Brennan, J. P.; Schaeffer, R.; Davison, A.; Wreford, S. S. *J. Chem. Soc., Chem. Commun.* **1973**, 354. (e) Shore, S. G. "Abstracts of Papers", 19th International Conference on Coordination Chemistry, Prague, Czechoslovakia, Sept 1978. (f) Greenwood, N. N.; Hails, M. J.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1980**, 37. (g) Greenwood, N. N.; McGinnety, J. A.; Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 989. (h) Guggenberger, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 114.

(5) In the known mercury complexes of the *nido*-$B_{10}H_{12}^{2-}$ ligand,[6] Hg is evidently η^4-coordinated to the cage, and in the complexes of *nido*-$C_2B_9H_{11}^{2-}$ and *closo*-$C_2B_{10}H_{11}^-$ it is η^1-coordinate (σ bonded).[7,8] A partially characterized complex formulated as μ-(C_6H_5Hg)-2,3-$C_2B_4H_7$ was reported several years ago.[9]

(6) (a) Greenwood, N. N.; Thomas, B. S.; Waite, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 299. (b) Greenwood, N. N.; Sharrocks, D. N. *J. Chem. Soc. A* **1969**, 2334. (c) Greenwood, N. N. *Pure Appl. Chem.* **1977**, *49*, 791.

0020-1669/81/1320-0863\$01.00/0