Insertion of CO_2-like Molecules into the Platinum–Nitrogen Bond of $[Pt(PPh_3)_2(PhNO)]$: the *X*-Ray Structures of $[Pt\{ON(Ph)C(NPh)S\}(PPh_3)_2]$ and $[Pt\{ON(Ph)C(O)NPh\}(PPh_3)_2]$†

Francesco Demartin
Istituto di Chimica Strutturistica Inorganica and C.N.R. Center Via Venezian 21, 20133 Milano, Italy
Maddalena Pizzotti, Francesca Porta, and Sergio Cenini *
Dipartimento di Chimica Inorganica e Metallorganica and C.N.R. Center, Via Venezian 21, 20133 Milano, Italy

The *X*-ray structure determination of the insertion product of $[Pt(PPh_3)_2(PhNO)]$ (**1**) with PhN=C=S, $[Pt\{ON(Ph)C(NPh)S\}(PPh_3)_2]$ [monoclinic, space group $P2_1/n$, with a = 17.779(7), b = 15.297(3), c = 17.951(4) Å, β = 109.49(2)°, and Z = 4; R = 0.036 for 4 317 reflections with $I \geqslant 3\sigma(I)$] has now confirmed the previously proposed structure for this compound. However, the *X*-ray structure determination of the insertion product with PhN=C=O, $[Pt\{ON(Ph)C(O)NPh\}(PPh_3)_2]$ [orthorhombic, space group *Pbca*, with a = 25.303(8), b = 19.462(6), c = 17.451(5) Å, and Z = 8; R = 0.075 for 2 001 reflections with $I \geqslant 3\sigma(I)$], while having confirmed that a C–N bond is formed within the co-ordination sphere of the metal, has shown that the entering molecule is bonded to platinum *via* nitrogen and not oxygen, as previously suggested. The difference in reactivity of PhN=C=S and PhN=C=O with complex (**1**) is discussed.

We have previously reported on the reactivity of $[Pt(PPh_3)_2(PhNO)]$ (**1**), having a η^2-bonded nitroso ligand, with alkenes and alkynes,[1,2] and with carbon dioxide and CO_2-like molecules.[1,3] In all cases a C–N bond is formed within the co-ordination sphere of the metal, and this has already been confirmed by the *X*-ray structural determinations carried out on $[Pt\{ON(Ph)C(O)O\}(PPh_3)_2]$ (**2**)[1] and on $[Pt\{ON(Ph)C(CO_2Me)=C(CO_2Me)\}(PPh_3)_2]$ (**5**).[1,2] In the case of the PhN=C=S and PhN=C=O derivatives (**3**) and (**4**), bonding of the platinum to nitrogen and not to sulphur or oxygen should be considered.[4] This possibility appeared to be less likely in view of the fact that cyclohexylcarbodi-imide, $C_6H_{11}N=C=NC_6H_{11}$, did not react with compound (**1**).[3] On the other hand, the chemistry developed by Hoberg *et al.*[5] on the nickel(0) are well characterised, similar compounds have not derived by the attack at the C=N bond of the isocyanate. This situation prompted us to investigate the *X*-ray structures of the insertion products of PhN=C=X (X = S or O) into the platinum–nitrogen bond of (**1**).

Experimental

The complexes $[Pt\{ON(Ph)C(NPh)S\}(PPh_3)_2]$ (**3**) and $[Pt\{ON(Ph)C(O)NPh\}(PPh_3)_2]$ (**4**) have been obtained as previously reported.[3] The crystals employed for *X*-ray structure determination were obtained by slow diffusion of n-hexane into a chloroform [compound (**3**)] or dichloromethane [compound (**4**)] solution of the complexes, under a dinitrogen atmosphere.

The crystal data for compounds (**3**) and (**4**) are summarized in Table 1 together with some experimental details. The diffraction intensities were collected at room temperature on a CAD-4 diffractometer with Mo-K_α radiation (λ = 0.710 73 Å) and reduced to F_o values corrected for absorption by the empirical method described in ref. 6. Both structures were solved by Patterson and Fourier methods, and refined by full-matrix least-squares methods, the minimized function being $\Sigma w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/2F_oLp$.

The Enraf-Nonius SDP package of crystallographic programs was used with the analytical scattering factors, corrected for the real and imaginary components of anomalous dispersion, taken from ref. 7. The hydrogen atoms were placed in calculated positions (C–H 0.95 Å) and their contribution to the

Table 1. Crystal data and intensity collection parameters

Compound	(**3**)	(**4**)
Formula	$C_{49}H_{40}N_2OP_2PtS\cdot CHCl_3$	$C_{49}H_{40}N_2O_2P_2Pt\cdot CH_2Cl_2$
M	1 081.36	1 030.85
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbca*
a/Å	17.779(7)	25.303(8)
b/Å	15.297(3)	19.462(6)
c/Å	17.951(4)	17.451(5)
β/°	109.49(2)	
U/Å^3	4 602(5)	8 594(8)
Z	4	8
D_c/g cm^{-3}	1.561	1.593
μ(Mo-K_α)/cm^{-1}	34.06	35.39
Min. transmission factor	0.899	0.662
Crystal dimensions (mm)	0.3 × 0.13 × 0.17	0.25 × 0.25 × 0.05
ω-scan width (°)	1.3 + 0.35 tanθ	1.7 + 0.35 tanθ
θ range (°)	3—23	3—21
Octants of reciprocal space explored	$\pm h, +k, +l$	$+h, +k, +l$
Measured reflections	8 296	4 973
Unique observed reflections with $I > 3\sigma(I)$ (N_o)	4 317	2 001
Final R and R' indices	0.036, 0.042	0.075, 0.088
No. of variables (N_v)	356	252
Estimated standard deviation[b]	1.162	2.380

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$. [b] $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 2. Positional parameters of non-hydrogen atoms for $[\overline{\mathrm{Pt}\{\mathrm{ON(Ph)C(NPh)S}}\}(\mathrm{PPh}_3)_2]\cdot\mathrm{CHCl}_3$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.451 85(2)	0.130 30(2)	0.162 33(2)	C(121)	0.589 6(4)	0.288 0(5)	0.258 8(4)
S(1)	0.493 9(1)	0.004 9(1)	0.231 3(1)	C(122)	0.524 8(5)	0.330 3(6)	0.269 9(5)
Cl(1)	0.283 2(3)	0.139 1(4)	0.350 5(4)	C(123)	0.533 5(5)	0.408 7(7)	0.310 8(5)
Cl(2)	0.450 1(3)	0.126 4(4)	0.416 2(3)	C(124)	0.609 4(5)	0.443 6(7)	0.341 1(5)
Cl(3)	0.354 3(3)	−0.027 2(3)	0.390 4(3)	C(125)	0.674 6(5)	0.402 2(6)	0.334 8(5)
P(1)	0.575 8(1)	0.186 6(1)	0.203 3(1)	C(126)	0.665 2(5)	0.324 8(6)	0.293 7(5)
P(2)	0.384 3(1)	0.239 2(1)	0.076 6(1)	C(131)	0.615 3(4)	0.199 8(5)	0.121 7(5)
O(1)	0.343 4(3)	0.069 1(4)	0.126 8(4)	C(132)	0.589 2(5)	0.140 2(6)	0.061 6(5)
N(1)	0.397 2(4)	−0.136 8(5)	0.218 3(4)	C(133)	0.618 8(6)	0.143 1(7)	−0.003 1(6)
N(2)	0.337 3(4)	−0.009 7(4)	0.159 8(4)	C(134)	0.670 6(6)	0.206 9(8)	−0.004 4(6)
C(s)	0.368 4(7)	0.076 7(9)	0.355 9(7)	C(135)	0.697 2(6)	0.266 1(7)	0.054 0(6)
C(1)	0.404 1(5)	−0.054 1(5)	0.202 6(4)	C(136)	0.669 5(5)	0.263 0(6)	0.117 9(5)
C(11)	0.460 6(4)	−0.186 5(6)	0.267 7(5)	C(211)	0.413 1(4)	0.353 7(5)	0.088 4(4)
C(12)	0.515 4(5)	−0.155 7(6)	0.340 4(5)	C(212)	0.484 8(5)	0.378 9(6)	0.079 3(5)
C(13)	0.571 0(6)	−0.212 7(7)	0.386 9(6)	C(213)	0.508 0(5)	0.467 0(6)	0.090 0(5)
C(14)	0.575 5(6)	−0.296 7(7)	0.365 2(6)	C(214)	0.462 8(6)	0.527 5(7)	0.110 9(6)
C(15)	0.520 9(7)	−0.327 0(7)	0.294 4(7)	C(215)	0.393 4(6)	0.502 4(7)	0.120 9(6)
C(16)	0.464 8(6)	−0.272 6(6)	0.247 9(6)	C(216)	0.368 9(5)	0.415 8(6)	0.111 0(5)
C(21)	0.257 2(5)	−0.039 8(6)	0.131 7(5)	C(221)	0.280 5(4)	0.239 5(5)	0.073 3(4)
C(22)	0.230 5(5)	−0.104 8(8)	0.167 6(7)	C(222)	0.218 0(5)	0.239 1(5)	0.002 6(5)
C(23)	0.153 0(6)	−0.133 2(8)	0.137 9(8)	C(223)	0.139 4(5)	0.237 1(6)	0.002 0(5)
C(24)	0.098 2(5)	−0.093 0(9)	0.074 5(6)	C(224)	0.124 0(5)	0.238 0(7)	0.070 8(6)
C(25)	0.124 3(6)	−0.027 5(9)	0.041 4(6)	C(225)	0.186 8(6)	0.238 7(7)	0.143 3(6)
C(26)	0.202 2(5)	0.000 4(7)	0.067 5(6)	C(226)	0.264 2(5)	0.239 3(6)	0.144 1(5)
C(111)	0.650 0(4)	0.116 4(5)	0.272 2(4)	C(231)	0.382 0(4)	0.214 9(5)	−0.023 8(4)
C(112)	0.642 8(5)	0.104 1(6)	0.346 6(5)	C(232)	0.373 2(5)	0.280 1(6)	−0.079 4(5)
C(113)	0.696 6(5)	0.050 4(7)	0.402 8(5)	C(233)	0.375 3(5)	0.260 0(6)	−0.155 0(5)
C(114)	0.755 3(6)	0.009 1(7)	0.382 7(6)	C(234)	0.384 9(6)	0.175 3(7)	−0.174 1(6)
C(115)	0.764 8(6)	0.020 8(7)	0.311 6(6)	C(235)	0.389 9(6)	0.108 5(7)	−0.121 2(6)
C(116)	0.710 9(5)	0.074 6(6)	0.255 5(5)	C(236)	0.389 5(5)	0.129 4(6)	−0.044 9(5)

Table 3. Positional parameters of non-hydrogen atoms for $[\overline{\mathrm{Pt}\{\mathrm{ON(Ph)C(O)N}}\mathrm{Ph}\}(\mathrm{PPh}_3)_2]\cdot\mathrm{CH_2Cl_2}$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.229 39(5)	0.066 22(7)	0.146 51(6)	C(125)	0.095(1)	−0.082(2)	0.337(2)
P(1)	0.143 2(3)	0.052 9(5)	0.166 8(5)	C(126)	0.112(2)	−0.059(2)	0.268(2)
P(2)	0.257 0(4)	−0.005 3(5)	0.242 0(4)	C(131)	0.106(1)	0.136(2)	0.167(2)
O(1)	0.307(1)	0.088(1)	0.129(1)	C(132)	0.061(1)	0.148(2)	0.135(2)
O(3)	0.276(1)	0.202(1)	−0.021(1)	C(133)	0.033(2)	0.208(3)	0.152(3)
N(1)	0.225(1)	0.133(1)	0.060(1)	C(134)	0.060(2)	0.264(2)	0.188(2)
N(2)	0.316(1)	0.136(1)	0.071(2)	C(135)	0.109(2)	0.254(3)	0.213(2)
C(2)	0.266(1)	0.157(2)	0.029(2)	C(136)	0.140(2)	0.190(2)	0.209(2)
C(11)	0.178(1)	0.161(2)	0.017(2)	C(211)	0.330(1)	−0.010(2)	0.239(2)
C(12)	0.157(1)	0.117(2)	−0.040(2)	C(212)	0.351(1)	−0.048(2)	0.183(2)
C(13)	0.111(2)	0.145(2)	−0.081(2)	C(213)	0.412(1)	−0.057(2)	0.179(2)
C(14)	0.096(2)	0.213(2)	−0.072(2)	C(214)	0.439(2)	−0.022(2)	0.230(2)
C(15)	0.121(2)	0.252(2)	−0.018(2)	C(215)	0.416(2)	0.016(2)	0.292(2)
C(16)	0.161(1)	0.228(2)	0.031(2)	C(216)	0.361(2)	0.025(2)	0.299(2)
C(21)	0.368(2)	0.147(2)	0.061(2)	C(221)	0.242(1)	−0.090(1)	0.237(1)
C(22)	0.410(2)	0.108(3)	0.097(3)	C(222)	0.252(2)	−0.143(2)	0.296(2)
C(23)	0.460(3)	0.188(3)	0.082(3)	C(223)	0.241(2)	−0.213(2)	0.278(2)
C(24)	0.482(2)	0.175(3)	0.035(3)	C(224)	0.221(2)	−0.240(2)	0.211(2)
C(25)	0.443(2)	0.207(2)	−0.003(3)	C(225)	0.211(1)	−0.189(2)	0.153(2)
C(26)	0.383(2)	0.200(3)	0.011(3)	C(226)	0.219(1)	−0.117(2)	0.164(2)
C(111)	0.107(1)	−0.004(2)	0.102(2)	C(231)	0.239(1)	0.027(1)	0.334(1)
C(112)	0.057(2)	−0.016(2)	0.113(2)	C(232)	0.219(1)	−0.011(2)	0.402(2)
C(113)	0.031(2)	−0.067(3)	0.062(2)	C(233)	0.210(2)	0.025(2)	0.467(2)
C(114)	0.061(2)	−0.096(2)	0.001(2)	C(234)	0.219(2)	0.091(2)	0.488(2)
C(115)	0.111(2)	−0.080(2)	−0.010(2)	C(235)	0.242(1)	0.130(2)	0.417(2)
C(116)	0.139(1)	−0.033(2)	0.039(2)	C(236)	0.251(1)	0.098(1)	0.337(1)
C(121)	0.117(1)	0.013(2)	0.260(2)	Cl(1)	0.437(1)	0.284(2)	0.203(2)
C(122)	0.106(1)	0.060(2)	0.322(2)	Cl(2)	0.386(1)	0.212(2)	0.314(2)
C(123)	0.089(2)	0.032(2)	0.390(2)	C(s)	0.433(7)	0.158(9)	0.21(1)
C(124)	0.084(2)	−0.041(2)	0.397(2)				

structure factors was computed in the case of compound (**3**). The atomic co-ordinates for non-hydrogen atoms of both compounds are reported in Tables 2 and 3.

Results and Discussion

Perspective views of complexes (**3**) and (**4**) are shown in Figures 1 and 2 respectively. Selected interatomic distances and

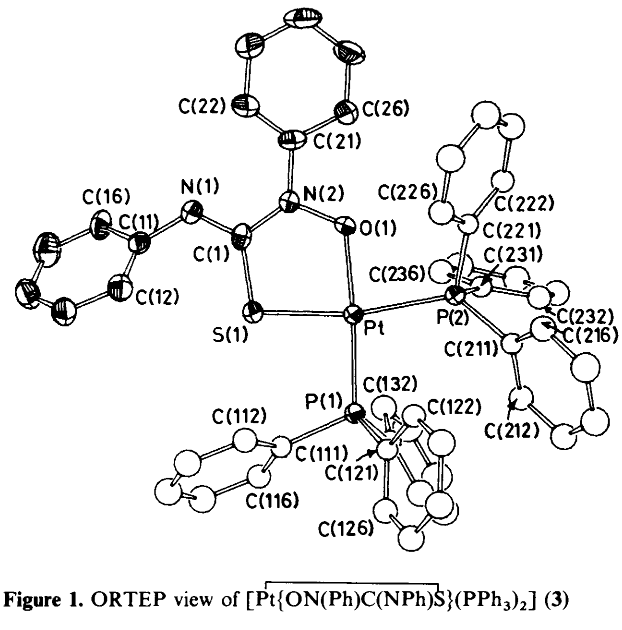


Figure 1. ORTEP view of $[\mathrm{Pt\{ON(Ph)C(NPh)S\}(PPh_3)_2}]$ (3)

angles are given in Table 4. For both molecules the bond angles around the square-planar platinum(II) atoms are unexceptional although it is worth noting that the P(1)–Pt–P(2) angle in (4) [96.5(2)°] is smaller than the corresponding one in (3) [100.17(7)°]. This appears to be related to the geometry of the two *cis* triphenylphosphine ligands which, in complex (4), are tightly interlocked by a 'quasi-graphite-like' stacking of the two phenyl rings C(121)–C(126) and C(231)–C(236) lying almost parallel at a distance close to a graphitic interaction. This feature has already been observed in other $\mathrm{Pt^{II}}$ complexes with *cis* triphenylphosphine ligands[8] and results in smaller P–Pt–P angles. The pattern of bond distances and angles around the metal atom in (3) is very close to that in $[\mathrm{Pt\{SN{=}C(C_6H_4CH_3\text{-}\mathit{p})O\}(PPh_3)_2}]$[9] with the Pt–P(2) distance longer than Pt–P(1) as a result of a higher *trans* influence of the sulphur-bonded isothiocyanate moiety.

The five-membered metallacycle displays a 'skew' conformation with the N(2) and C(1) atoms −0.11 and +0.4 Å respectively from the plane defined by the Pt, O(1), and S(1) atoms. The extent of distortion can be seen, for instance, from the torsional angle O(1)–N(2)–C(1)–S(1) which is 14.1°. The distribution of distances suggests fractional bond orders and delocalized electron density involving the chelate ring and extending also to N(1), C(11), and C(21) atoms. Major double-bond character is shown by the N(1)–C(1) interaction in compound (3) while the C(1)–S(1) bond length is slightly longer than the C–S distance in thiophene (1.74 Å).[10]

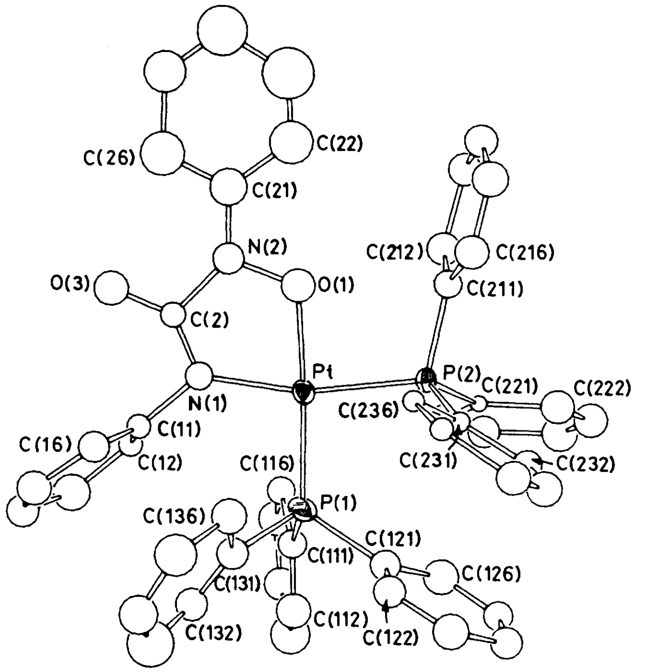


Figure 2. ORTEP view of $[\mathrm{Pt\{ON(Ph)C(O)NPh\}(PPh_3)_2}]$ (4)

The Pt–O(1) and Pt–N(1) distances in (4) can be compared with the values of 2.024(15) and 2.001(20) Å found in $[\mathrm{Pt\{NHN{=}C(C_6H_4NO_2\text{-}\mathit{p})O\}(PPh_3)_2}]$.[8] The difficulty of growing good single crystals of (4), suitable for *X*-ray structure analysis, and the partial twinning of the crystal studied are reflected in higher e.s.d.s on bond distances so that, although the essential features of the chelating ligand are clearly seen, a complete discussion is prevented. The C(2)–O(3) bond length [1.27(2) Å], compared with the values of 1.23 Å usually found for a >C=O distance in ketones and 1.26 Å in urea,[10] indicates a prevalence of double bond character, in agreement with the i.r. $\nu_{\mathrm{C=O}}$ frequency observed (1 608 cm^{-1}).

In order to explain the different reactivity of PhN=C=S (addition to the C=S bond) and of PhN=C=O (addition to the C=N bond) with respect to compound (1), we considered the

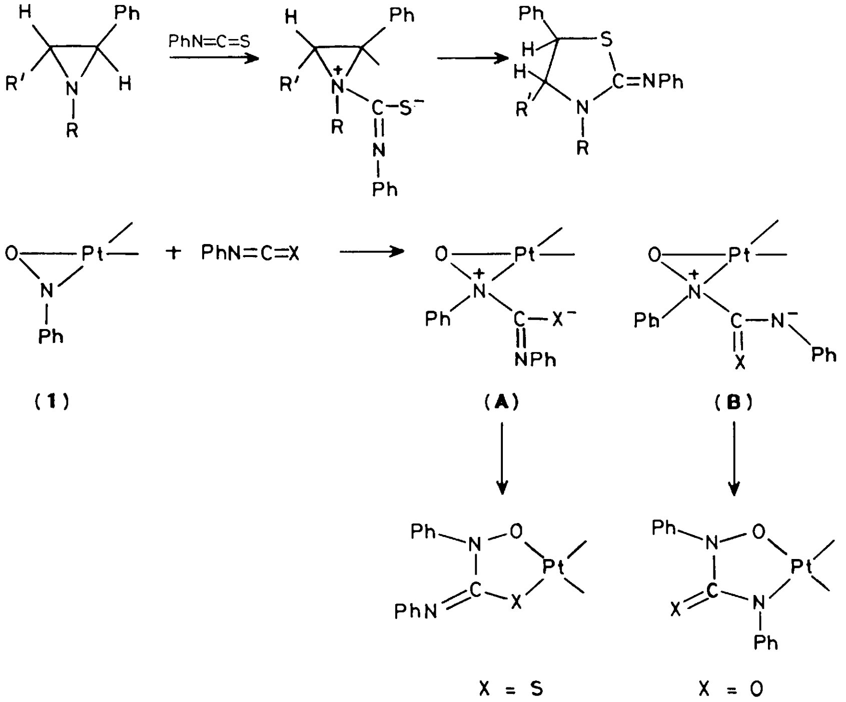
Table 4. Selected bond distances (Å) and angles (°)

(*a*) For $[\mathrm{Pt\{ON(Ph)C(NPh)S\}(PPh_3)_2}]$ (3)

Pt–P(1)	2.248(2)	N(2)–C(21)	1.420(10)
Pt–P(2)	2.314(2)	N(2)–C(1)	1.360(9)
Pt–O(1)	2.044(5)	C(1)–S(1)	1.755(8)
Pt–S(1)	2.270(2)	C(1)–N(1)	1.310(9)
O(1)–N(2)	1.364(8)	N(1)–C(11)	1.403(10)
P(1)–Pt–P(2)	100.17(7)	N(2)–C(1)–S(1)	116.5(6)
P(1)–Pt–S(1)	92.10(7)	C(1)–S(1)–Pt	99.9(3)
P(2)–Pt–O(1)	84.03(15)	O(1)–N(2)–C(21)	110.4(6)
O(1)–Pt–S(1)	83.56(15)	C(21)–N(2)–C(1)	128.4(7)
P(1)–Pt–O(1)	175.25(16)	N(2)–C(1)–N(1)	118.5(8)
P(2)–Pt–S(1)	167.07(7)	S(1)–C(1)–N(1)	125.0(6)
Pt–O(1)–N(2)	118.2(4)	C(1)–N(1)–C(11)	123.2(7)
O(1)–N(2)–C(1)	120.4(6)		

(*b*) For $[\mathrm{Pt\{ON(Ph)C(O)NPh\}(PPh_3)_2}]$ (4)

Pt–P(1)	2.225(6)	N(2)–C(21)	1.36(3)
Pt–P(2)	2.281(6)	N(2)–C(2)	1.53(3)
Pt–O(1)	2.024(17)	C(2)–O(3)	1.27(2)
Pt–N(1)	1.996(17)	C(2)–N(1)	1.26(3)
O(1)–N(2)	1.41(2)	N(1)–C(11)	1.51(3)
P(1)–Pt–P(2)	96.5(2)	N(2)–C(2)–N(1)	112.1(19)
P(1)–Pt–N(1)	98.0(7)	C(2)–N(1)–Pt	121.5(17)
P(2)–Pt–O(1)	86.5(5)	O(1)–N(2)–C(21)	111.3(24)
O(1)–Pt–N(1)	78.9(8)	C(21)–N(2)–C(2)	135.3(25)
P(1)–Pt–O(1)	174.8(5)	N(2)–C(2)–O(3)	110.4(24)
P(2)–Pt–N(1)	165.5(7)	O(3)–C(2)–N(1)	136.7(26)
Pt–O(1)–N(2)	114.0(14)	C(2)–N(1)–C(11)	107.1(18)
O(1)–N(2)–C(2)	112.9(20)	C(11)–N(1)–Pt	131.3(16)



Scheme. R′ = aroyl, R = Me

similarity between the metallaoxaziridine (**1**) and organic aziridines.[11]

Aryl isothiocyanates react readily with 3-aroylaziridines to yield 5-iminothiazolidines, corresponding to cycloaddition across the C=S bond, while with 2-(alkoxycarbonyl)aziridines the addition is exclusively at the C=N bond.[11] The formation of the thiazolidines in the former case is accompanied by the formation of 2-(arylimino)thiazolidines, which results from nucleophilic attack by the aziridine nitrogen on the carbon atom of the isothiocyanate group and ring expansion (Scheme).

Reaction of 2-(alkoxycarbonyl)aziridines with methyl- and phenyl-isocyanates results in regiospecific addition to the C=N bond exclusively. It is difficult to predict the course of the 1,3-dipolar cycloaddition reactions [11] and, at the moment, it is even more difficult to predict the course of the reaction of compound (**1**) with isocyanates. However if nucleophilic attack by nitrogen on the carbon atom of the RNCX molecules is operating even in the case of compound (**1**), intermediates such as (**A**) and (**B**) (Scheme) can explain the different regioselectivity exhibited by (**1**) with respect to PhN=C=S [intermediate (**A**)] and PhN=C=O [intermediate (**B**)].

The order of reactivity for reaction of nucleophiles with platinum(II) complexes cannot be predicted from the basicities of the nucleophiles.[12] Our results seem to suggest that the reactivity for ring closure with platinum follows the order: $RS^- > R_2N^- > RO^-$. Thus, on the basis of the previous discussion, even the product obtained from $[Pt(PPh_3)_2(O_2)]$ and PhN=C=O [3] should now be reformulated as $[\overline{Pt\{O_2C(O)N}Ph\}(PPh_3)_2]$.

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