

Phosphine σ -sydnonyl complexes of Ni, Pd, and Pt

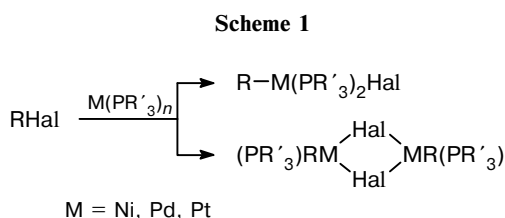
V. N. Kalinin,* F. M. She, V. N. Khandozhko, and P. V. Petrovskii

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, Moscow 117813, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: vkalin@ineos.ac.ru

3-R'-4-Bromosydones **1** (R' = Me) and **2** (R' = Ph) react with complexes $M(PR_3)_n$ (M = Ni, Pd, Pt) to form mononuclear phosphine σ -sydnonyl d^8 -complexes of *trans*-configuration $MBr(3-R'\text{-sydnon-4-yl})(PR_3)_2$: **3**, **4** (M = Ni, R' = Ph); **5** (M = Pd, R' = Me); **6a** (M = Pd, R' = Ph); **7** (M = Pt, R' = Ph). In the reaction of bromosydnone **2** with $Pd(PPh_3)_4$, the *cis*-complex $PdBr(3\text{-Ph-sydnon-4-yl})(PPh_3)_2$ (**6b**) is formed initially; **6b** rearranges in solution to give *trans*-complex **6a**. On heating in THF, complex **6a** is converted into the binuclear $[PdBr(3\text{-phenylsydnon-4-yl})(PPh_3)]_2$ complex (**8**). The reaction of 4-chloromercurio-3-phenylsydnone (**10**) with $Ni(PEt_3)_4$, $Pd(PPh_3)_4$, and $Pt(PPh_3)_4$ gives mononuclear $NiCl(3\text{-phenylsydnon-4-yl})(PEt_3)_2$ complex (**11**), binuclear $[PdCl(3\text{-phenylsydnon-4-yl})(PPh_3)]_2$ complex (**14**), and *cis*- and *trans*-bimetallic $PtCl(3\text{-phenylsydnon-4-ylmercurio})(PPh_3)_2$ complexes **15a** and **15b**, respectively. UV irradiation of **15a** and **15b** in a benzene solution induces redox demercuration to yield the $PtCl(3\text{-phenylsydnon-4-ylcarbonyl})(PPh_3)_2$ complex (**16**). In carbonylation of complexes **3**, **6**, and **7**, CO insertion into the M—C bond occurred to form the corresponding acyl derivatives $MBr(3\text{-phenylsydnon-4-ylcarbonyl})(PR_3)_2$ (**17–19**).

Key words: sydnones, nickel, palladium, platinum, σ -complexes, oxidative addition, carbonylation, redox demercuration.

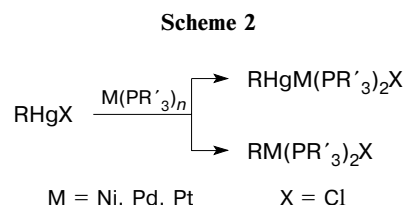
One of the methods for the preparation of heterocyclic derivatives with C—M σ -bonds (M is a transition metal) is oxidative addition of heteryl halides to zerovalent Ni, Pd, and Pt phosphine complexes.¹ Depending on the nature of the metal, reactant ratio, and reaction conditions, either mono- or binuclear complexes are formed (Scheme 1).



This method has been used successfully to prepare a number of σ -complexes by reactions of Ni^0 with 8-chloroquinoline,² Pd^0 with 2-chloro-6-X-pyridines (X is Cl, Br, I), 2-chlorobenzothiazole³ or 2-chloropyrazine,⁴ and Pt^0 with 2-chloro- or 2,6-dichloropyridine.⁵

Organomercury compounds can also react with zerovalent nickel, palladium, and platinum complexes to give either mono- or bimetallic complexes, depending on the nature of organic radicals^{6,7} (Scheme 2).

The formation of stable bimetallic complexes of these three metals is facilitated by the strong electron-withdrawing effect of the organic substituent R. Stabilization of bimetallic complexes is attained due to perfluorinated substituents.^{8,9} In the case of platinum, this stabilization



can also be achieved by using sterically hindered derivatives, namely, duryl, mesityl, indolyl, carboranyl, and manganese- and rheniumcyclopentadienyl(tricarbonyl) derivatives.^{10,11} The absence of the above-noted factors in the bimetallic Hg—M complexes (M = Ni, Pd, Pt) results in redox demercuration giving rise to a monometallic complex.

In this study, using mesoionic heterocycles, sydnones, we prepared the first representatives of mesoionic compounds containing a C—M σ -bond (M = Ni, Pd, Pt), studied the behavior of these compounds toward carbonylation, and also synthesized a stable bimetallic sydnonyl platinum complex with a Pt—Hg σ -bond. The tentative results of this study were reported previously.^{12,13}

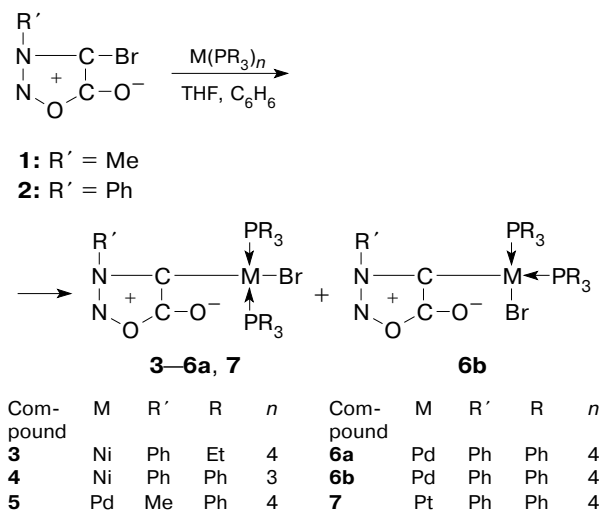
Results and Discussion

Reaction of 4-bromosydones with zerovalent Ni, Pd, and Pt phosphine complexes

We investigated oxidative addition of 4-bromo-3-methylsydnone (**1**) and 4-bromo-3-phenylsydnone (**2**)

to zerovalent nickel, palladium, and platinum phosphine complexes (Scheme 3).

Scheme 3



As the starting compounds, we used Ni(PEt₃)₄, Ni(PPh₃)₃, Pd(PPh₃)₄, and Pt(PPh₃)₄. In each case, except for the reaction of **2** with Pd(PPh₃)₄, the oxidative addition of 4-bromosydnone occurred smoothly and yielded only the *trans*-isomer MBr(3-R'-sydnon-4-yl)(PR₃)₂. The reactions took place at ~20 °C; for Ni, they required 2 h (R = Et) and 4 h (R = Ph), for Pd, the reaction times were 0.25 h (R' = Ph) and 2 h (R' = Me), and for Pt, the duration was 0.5 h. In the oxidative addition of 4-bromo-3-phenylsydnone **2** to Pd(PPh₃)₄, the formation of rather stable *cis*-isomer **6b** was detected apart from the *trans*-isomer **6a**.

σ-Sydnonyl nickel compounds **3** and **4** are mononuclear complexes, whose ³¹P NMR spectra contain one narrow singlet at 13.19 and 20.76 ppm, respectively, indicating the *trans*-arrangement of the phosphine ligands around the nickel atom. Nickel complexes **3** and **4** are dark-brown crystalline compounds, stable against atmospheric oxygen in the solid state and soluble in benzene.

The oxidative addition of 4-bromo-3-methylsydnone (**1**) to Pd(PPh₃)₄ affords *trans* complex **5**; this was confirmed by the ³¹P NMR spectrum, which exhibits one singlet at 17.53, pointing to equivalence of phosphine ligands. The ¹H NMR spectrum contains a singlet at 3.17 ppm and a multiplet at about 7.5 ppm. The ratio of the integral intensities of the ¹H NMR signals, equal to 1 : 10, confirms the formation of a mononuclear complex.

However, a mixture of *trans* (**6a**) and *cis* (**6b**) isomers is formed in the reaction of 4-bromo-3-phenylsydnone (**2**) with Pd(PPh₃)₄. The ³¹P NMR spectrum contains a singlet at 21.50 ppm and an AB-quartet (δ_A = 19.20, δ_B = 29.39, J = 21.5 Hz), assigned to complexes **6a** and **6b**. The **6a** to **6b** isomer ratio determined from the ratio of the integral intensities of these signals depends on the

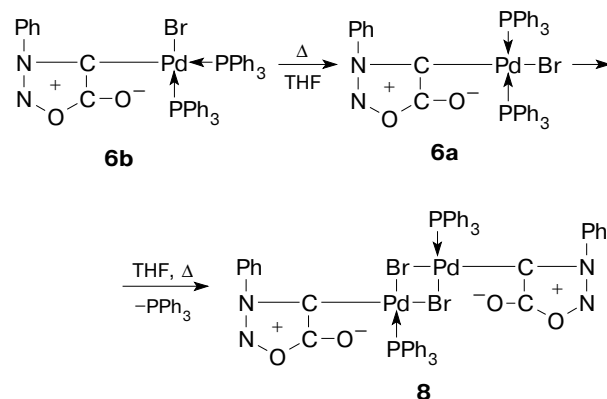
solvent used in the reaction (1 : 6.7 in THF and 1.6 : 1 in benzene). The presence of isomers is confirmed by the IR spectra, which exhibit bands for Pd—Br stretching vibrations in two compounds, at 244 and 216 cm⁻¹. At room temperature, the isomer ratio in the solution remains virtually unchanged, and when the temperature is raised, the amount of *trans*-isomer **6a** gradually increases.

It should be noted that oxidative addition of organic halides in which halogen is attached to an sp²-hybridized carbon atom to M⁰ complexes (M = Ni, Pd, Pt) gives normally *trans*-compounds. In the case of monodentate ligands, the formation of *cis*-isomers as unstable intermediates rapidly rearranging into *trans*-isomers was postulated. Stable palladium complexes with substituted uracil^{14,15} and 3,5-dichlorotriphenyl¹⁶ ligands having the *cis*-structure were reported as exceptions.

Palladium σ-sydnonyl complexes **5** and **6a,b** are yellow crystalline solids stable in air and in the light. Complex **5** is readily soluble, while **6a,b** are poorly soluble in THF and benzene.

Refluxing of an isomer mixture of palladium complexes **6a,b** in THF or benzene gives rise to a binuclear complex, *trans*-bis[bromo(triphenylphosphine)(3-phenylsydnon-4-yl)palladium] (**8**) (Scheme 4).

Scheme 4



This reaction was studied by ³¹P NMR spectroscopy. Samples for recording the spectra in THF were taken directly during the reaction. The presence of particular complexes in the reaction mixture was judged from the above-mentioned signals typical of *trans*- (**6a**) and *cis*-isomers (**6b**) and the newly formed singlet at 22.26 ppm assigned to binuclear *trans*-complex **8**. The ratio of these complexes in the reaction mixture was determined from the integral intensities of the signals. Initially, *cis*-isomer **6b** rearranges into *trans*-isomer **6a**; when the remaining amount of **6b** is ~3–5%, **6a** starts to transform into binuclear complex **8**, i.e., at this instant, all three compounds are detected in the solution. Within 30 min after refluxing has started, only complexes **6a** and **8** in ~2 : 1 ratio remain in the reaction mixture, and 2 h later, the solution contains only binuclear complex **8**.

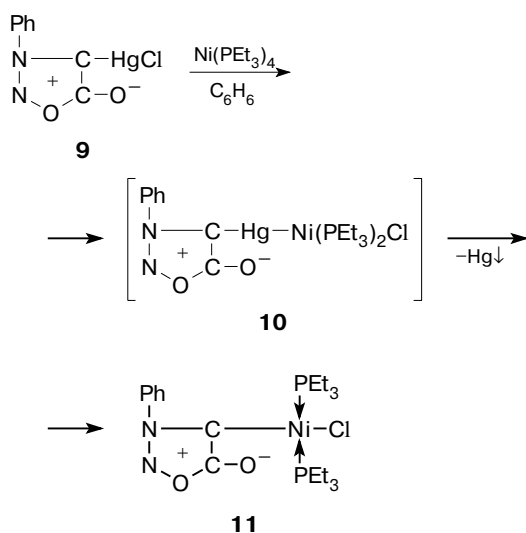
Our attempts to isolate *trans*-isomer **6a** in a pure state failed. Binuclear complex **8** is a yellow crystalline compound stable in air and, unlike complexes **6a** and **6b**, readily soluble in THF and benzene.

4-Bromo-3-phenylsydnone (**2**) reacts with $\text{Pt}(\text{PPh}_3)_4$ to give mononuclear complex **7**. Its ^{31}P NMR spectrum contains a singlet at 11.60 ppm with satellites caused by the ^{195}Pt – ^{31}P spin-spin coupling with a constant of 3573 Hz, which implies *trans*-arrangement of the phosphine ligands. The IR spectrum displays Pt–Br stretching vibrations at 209 cm^{-1} ; the absorption band for the sydnone carbonyl group is shifted from 1700 cm^{-1} , typical of analogous nickel and palladium complexes, to the region of 1500 cm^{-1} , which is apparently due to partial coordination of the exocyclic oxygen atom of sydnone to platinum. Complex **7** is a white crystalline solid, stable in air and in the light and poorly soluble in THF.

Reaction of 4-chloromercurio-3-phenylsydnone with zerovalent Ni, Pd, Pt phosphine complexes

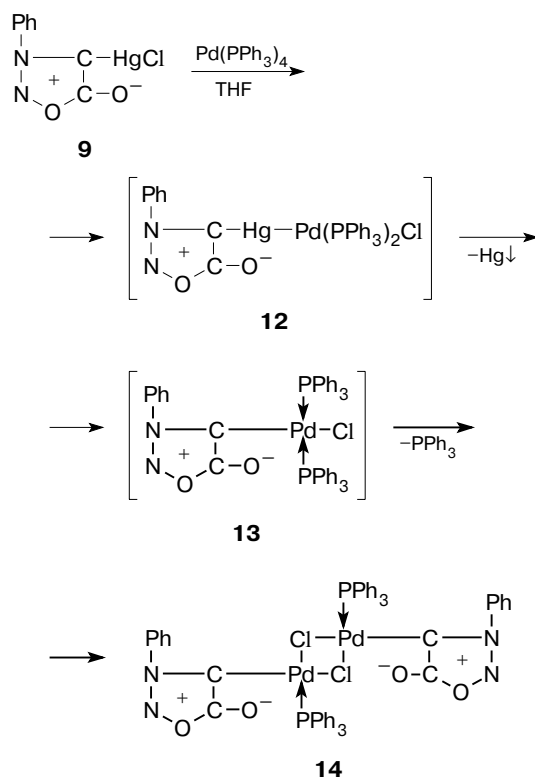
The 3-phenylsydnon-4-yl radical exhibits a substantial electron-withdrawing effect.¹⁷ Therefore, we attempted to prepare bimetallic sydnonyl complexes containing a Hg–M bond (M = Ni, Pd, Pt) by the reaction of 4-chloromercurio-3-phenylsydnone (**9**) with Ni^0 , Pd^0 , and Pt^0 phosphine complexes. However, the stabilizing effect of the sydnon-4-yl substituent was found to be insufficient for the formation of stable bimetallic complexes of nickel and palladium. The reaction of **9** with $\text{Ni}(\text{PEt}_3)_4$ gave rise to *trans*-chlorobis(triethylphosphine)(3-phenylsydnon-4-yl)nickel (**11**), resulting from redox demercuration of intermediate **10** (Scheme 5). Complex **11** is similar in properties to nickel bromo complexes **3** and **4**. The ^{31}P NMR spectrum of complex **11** contains a singlet at 13.19 ppm.

Scheme 5



Binuclear complex **14**, similar to binuclear palladium complex **8**, was obtained in the reaction of **9** with $\text{Pd}(\text{PPh}_3)_4$ (Scheme 6).

Scheme 6

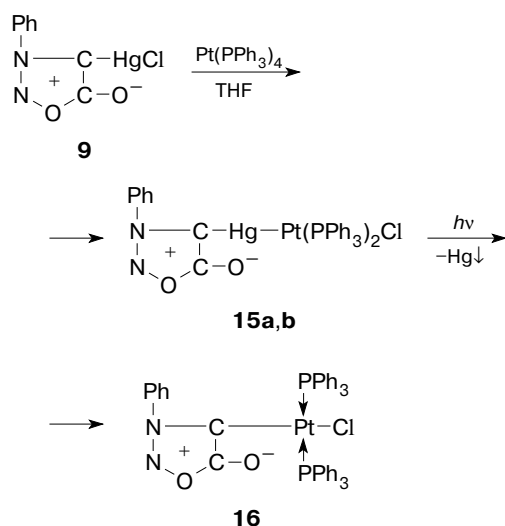


Interesting results were obtained in a ^{31}P NMR study of this reaction. The spectrum of a sample taken from the reaction mixture in benzene 15 min after the beginning of the reaction displays a singlet at 23.47 ppm and an AB-quartet ($\delta_A = 21.05$, $\delta_B = 31.50$, $J = 21.3\text{ Hz}$), assigned to the *trans*- and *cis*-isomers of the bimetallic complex **12**; the ratio of the integral intensities of these signals is 1 : 2.3. Apart from these signals, the spectrum contains a weak singlet at 21.93 ppm, close to the singlet in the spectrum of mononuclear palladium bromo *trans*-complex **6a** (21.50 ppm), which was attributed to the mononuclear chloro complex **13**. Subsequently, the signals for complexes **12** start decreasing, while that for **13** starts increasing. After 1 h, the signals of *trans*- and *cis*-complexes **12** disappear, while the singlet at 21.93 ppm persists. A new singlet close to the singlet in the spectrum of binuclear bromo complex **8** (22.26 ppm) appears at 22.96 ppm; it was assigned to binuclear chloro *trans*-complex **14**. Within 5 h after the beginning, only singlet due to complex **14** is found in the spectrum.

The reaction of **9** with $\text{Pt}(\text{PPh}_3)_4$, unlike the reactions with $\text{Ni}(\text{PEt}_3)_4$ and $\text{Pd}(\text{PPh}_3)_4$, gives rise to a mixture of stable bimetallic complexes *trans*- (**15a**) and *cis*-chlorobis(triethylphosphine)(3-phenylsydnon-4-ylmercurio)platinum (**15b**) (Scheme 7). The isomer ratio

was determined from the ^{31}P NMR spectrum. The singlet at 13.93 ppm with satellites caused by the ^{195}Pt — ^{31}P spin-spin coupling with a constant of 3679.9 Hz was assigned to the *trans*-isomer **15a**. The AB-quartet ($\delta_{\text{A}} = 12.56$, $\delta_{\text{B}} = 19.42$, $J = 14.5$ Hz) with satellites due to the ^{195}Pt — ^{31}P spin-spin coupling with $J(^{195}\text{Pt}$ — $^{31}\text{P}_{\text{A}}) = 2414.7$ Hz, $J(^{195}\text{Pt}$ — $^{31}\text{P}_{\text{B}}) = 2996.4$ Hz, was attributed to the nonequivalent phosphine ligands in *cis*-isomer **15b**. The integral intensity of the signals indicates that the *cis*- to *trans*-isomer ratio amounts to 1 : 2.7. The **15a** and **15b** mixture is a white crystalline solid poorly soluble in THF.

Scheme 7



The results confirm the general trend: in the series of Ni, Pd, and Pt complexes with the 3-phenylsydnon-4-yl group, the bimetallic platinum complex is the most stable, as has been also noted previously for complexes with other organic substituents.^{6–8,18}

Complexes **15a** and **15b** slowly decompose in a THF solution. This process is markedly accelerated on exposure to ultraviolet radiation. This gives a mononuclear chloro *trans*-complex **16**, an analog of the platinum bromo complex **7**. The ^{31}P NMR spectrum of this complex contains a singlet at 12.11 ppm with satellites caused by the ^{195}Pt — ^{31}P spin-spin coupling with a constant of 3560 Hz.

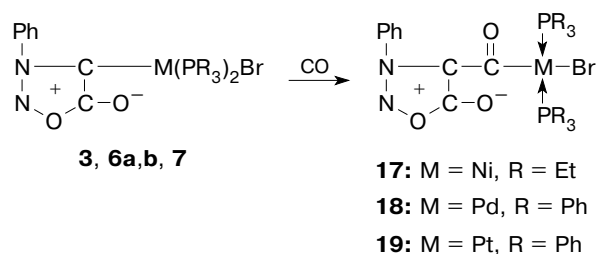
Carbonylation of σ -sydnonyl complexes of Ni, Pd, and Pt

It is known that the products of oxidative addition of nickel triad metals can be carbonylated by CO, which is inserted into the C—M bond to give the corresponding acyl complexes.^{19–22} The stability of acyl complexes decreases in the series Ni > Pd > Pt.

Carbonylation of nickel σ -sydnonyl complex **3** on passing CO through a suspension of **3** in hexane at room temperature results in an acyl complex,

namely, *trans*-bromobis(triethylphosphine)(3-phenylsydnon-4-ylcarbonyl)nickel (**17**) (Scheme 8).

Scheme 8



The isomer mixture of palladium complexes **6a**, **6b** and platinum complex **7** were carbonylated in an autoclave under a CO pressure of $25 \cdot 10^5$ Pa at 50 °C in THF. This also gave acyl complexes, *trans*-bromobis(triphenylphosphine)(3-phenylsydnon-4-ylcarbonyl)palladium (**18**) and *trans*-bromobis(triphenylphosphine)(3-phenylsydnon-4-ylcarbonyl)platinum (**19**).

The nickel acyl complex **17** was isolated as a dark-yellow crystalline solid; the attempt to recrystallize this product failed because it was readily decarbonylated, similarly to arylacyl complexes.²³ The sydnonyl acyl complexes of palladium **18** and platinum **19** are stable only in solutions saturated with carbon monoxide. We were unable to isolate these acyl complexes in a pure state, although rather stable acyl complexes of palladium with pyridyl and thienyl⁹ ligands and a platinum complex with an aroyl²² ligand are known. The formation of acyl complexes **17**–**19** was confirmed by the IR spectra. In the case of nickel and palladium, the IR spectra exhibit an absorption band at about 1770 cm^{-1} , which is missing from the spectra of starting complexes **3**, **6**, and **7**. In the case of palladium complex, the ^{31}P NMR spectrum points to the formation of only *trans* acyl complex **18**, although the starting compound used in carbonylation was a mixture of isomers **6a** and **6b**; this confirms the previously established influence of acyl groups promoting the predominant formation of *trans*-isomers for related acyl complexes.²¹

In the IR spectrum of platinum acyl complex **19**, the absorption band shifts from the region of 1500 cm^{-1} observed for the starting complex **7** to 1715 cm^{-1} , pointing to the absence of coordination of the exocyclic sydnone oxygen atom to platinum. Two new absorption bands appear at 1728 cm^{-1} and 1780 cm^{-1} ; they were assigned to the carbonyl group of the acyl complex. The presence of two absorption bands is, apparently, due to the presence of conformers resulting from hindered rotation around the C—C bond in α -substituted acyl complex **19**; this is similar to the platinum aroyl complex **22**.

Experimental

^1H and ^{31}P NMR spectra were recorded on a Bruker WP-200SY spectrometer (200.13 MHz and 81.01 MHz),

IR spectra were measured on UR-20 (KBr pellets) and Bruker IFS-113v (mineral oil) instruments. The compounds Ni(PPh₃)₃,²⁴ Ni(PEt₃)₄,²⁵ Pd(PPh₃)₄,²⁶ Pt(PPh₃)₄,²⁷ 4-bromo-3-methyl-sydnone,²⁸ 4-bromo-3-phenyl-sydnone,²⁸ and 4-chloromercurio-3-phenylsydnone²⁹ were prepared by known procedures. The reactions were carried out in anhydrous solvents prepared by distillation from benzophenone ketyl under argon.

trans-Bromobis(triethylphosphine)(3-phenylsydnone-4-yl)nickel (3). A suspension of 4-bromo-3-phenylsydnone (1.25 g, 5.20 mmol) in 10 mL of benzene was added to a suspension Ni(PEt₃)₄ (2.75 g, 5.17 mmol) in 20 mL of benzene. The reaction mixture was stirred for 2 h at ~20 °C. The solution thus formed was concentrated to dryness and the residue was diluted with 20 mL of ether. The orange compound that formed was filtered off, washed with ether, and dried *in vacuo* to give 1.27 g (69%) of complex **3**, m.p. 129–131 °C. ³¹P NMR (CHCl₃), δ : 13.19 (s). IR, ν/cm^{-1} : 1705. Found (%): N, 5.11; P, 11.30; Br, 14.58. C₂₀H₃₅BrN₂NiO₂P₂. Calculated (%): N, 5.27; P, 11.50; Br, 14.5.

trans-Bromobis(triphenylphosphine)(3-phenylsydnone-4-yl)nickel (4). A suspension of 4-bromo-3-phenylsydnone (0.66 g, 2.74 mmol) in 10 mL of toluene was added to a suspension of Ni(PPh₃)₃ (2.97 g, 3.51 mmol) in 20 mL of toluene at –40 °C. The reaction mixture was stirred for 4 h at ~20 °C and concentrated. The resulting brown compound was filtered off, washed with ether, and dried *in vacuo* to give 1.27 g (58%) of compound **4**, m.p. 137–135 °C. ³¹P NMR (CHCl₃), δ : 20.76 (s). IR, ν/cm^{-1} : 1705. Found (%): C, 64.07; H, 4.24; N, 3.40. C₄₄H₃₅BrN₂NiO₂P₂. Calculated (%): C, 63.48; H, 4.34; N, 3.63.

trans-Bromobis(triphenylphosphine)(3-methylsydnone-4-yl)palladium (5). At ~20 °C, Pd(PPh₃)₄ (2.43 g, 2.1 mmol) was added to a solution of 4-bromo-3-methylsydnone (0.38 g, 2.1 mmol) in 50 mL of THF. The reaction mixture was stirred for 1 h, then the solvent was evaporated, and the yellow residue was recrystallized from a chloroform–hexane mixture (1 : 1) and dried *in vacuo* to give 1.11 g (65%) of compound **5**, m.p. 168–170 °C. ¹H NMR (CDCl₃), δ : 3.17 (s, 3 H, Me); 7.38–7.62 (m, 30 H, Ar). ³¹P NMR (CDCl₃), δ : 17.53 (s). IR, ν/cm^{-1} : 1700. Found (%): C, 57.82; N, 3.46; P, 7.66. C₃₉H₃₃BrN₂O₂P₂Pd. Calculated (%): C, 57.59; N, 3.74; P, 7.34.

trans-Bromobis(triphenylphosphine)- (6a) and cis-bromobis(triphenylphosphine)(3-phenylsydnone-4-yl)palladium (6b). At ~20 °C, Pd(PPh₃)₄ (2.43 g, 2.1 mmol) was added with stirring to a solution of 4-bromo-3-phenylsydnone (0.51 g, 2.1 mmol) in 50 mL of THF or benzene. After 20 min, the yellow precipitate was filtered off, washed with 40 mL of THF or benzene, and dried *in vacuo* to give 1.59 g (87%) of a mixture of *trans*- (**6a**) and *cis*-isomers (**6b**). ³¹P NMR (CDCl₃), δ : 19.20, 29.39 (both d, $J = 21.5$ Hz), 21.50 (s). IR, ν/cm^{-1} : 216, 244, 1700. Found (%): C, 60.62; H, 4.18; N, 3.21; Br, 9.18. C₄₄H₃₅BrN₂O₂P₂Pd. Calculated (%): C, 60.83; H, 4.06; N, 3.07; Br, 9.13.

trans-Bromobis(triphenylphosphine)(3-phenylsydnone-4-yl)platinum (7). At ~20 °C, Pt(PPh₃)₄ (2.61 g, 2.1 mmol) was added with stirring to a solution of 4-bromo-3-phenylsydnone (0.51 g, 2.1 mmol) in 50 mL of THF. After 30 min, the white precipitate was filtered off, washed with 40 mL of THF or benzene, and dried *in vacuo* to give 1.53 g (76%) of compound **7**, m.p. 281–283 °C. ³¹P NMR (CDCl₃), δ : 11.60 (s, $J(^{195}\text{Pt}-^{31}\text{P}) = 3573$ Hz). IR, ν/cm^{-1} : 209, 1705. Found (%): C, 55.00; H, 3.65; P, 6.46. C₄₄H₃₅BrN₂O₂P₂Pt. Calculated (%): C, 55.05; H, 3.89; P, 6.51.

trans-Bis[bromo(triphenylphosphine)(3-phenylsydnone-4-yl)palladium] (8). A suspension of an isomer mixture **6a** and **6b** (1.83 g, 2.1 mmol) in THF was refluxed for 1.5 h until the

precipitate completely dissolved and for an additional 1 h. The reaction mixture was cooled to ~20 °C and the solvent was evaporated *in vacuo*. The resulting yellow precipitate was dissolved in chloroform, hexane was added, and the resulting precipitate was filtered off and dried *in vacuo* to give 2.00 g (78%) of compound **8**, m.p. 149–151 °C. ³¹P NMR (THF), δ : 22.26 (s). Found (%): N, 4.59; P, 5.09; Br, 13.12. C₅₂H₄₄Br₂N₄O₄P₂Pd₂. Calculated (%): N, 4.12; P, 5.19; Br, 13.48.

trans-Chlorobis(triethylphosphine)(3-phenylsydnone-4-yl)nickel (11). A suspension of 4-chloromercurio-3-phenylsydnone (1.53 g, 3.84 mmol) in 10 mL of benzene was added to a solution of Ni(PEt₃)₄ (2.04 g, 3.84 mmol) in 10 mL of benzene. The reaction mixture was stirred for 20 h at ~20 °C. Then the precipitated metallic mercury was filtered off and the filtrate was concentrated to dryness. The residue was diluted with 20 mL of ether. The light-brown powder that crystallized was filtered off. The filtrate was concentrated to dryness and the residue was diluted with 10 mL of pentane. The orange crystalline precipitate was filtered off, washed with pentane, and dried *in vacuo* to give 1.08 g (57%) of compound **11**, m.p. 103–104 °C. ³¹P NMR (CHCl₃), δ : 13.19 (s). Found (%): C, 47.88; H, 7.02; P, 12.30. C₂₀H₃₅ClN₂NiO₂P₂. Calculated (%): C, 47.51; H, 6.92; P, 12.31.

trans-Bis[chloro(triphenylphosphine)(3-phenylsydnone-4-yl)palladium] (14). Pd(PPh₃)₄ (4.44 g, 3.84 mmol) was added to a suspension of 4-chloromercurio-3-phenylsydnone (1.53 g, 3.84 mmol) in 20 mL of benzene. The reaction mixture was stirred for 5 h at ~20 °C. The precipitated metallic mercury was filtered off and the filtrate was concentrated to dryness. The residue was dissolved in chloroform and treated with hexane. The light-yellow precipitate thus formed was filtered off and dried *in vacuo* to give 4.36 g (51%) of compound **14**, m.p. 149–151 °C. ³¹P NMR (C₆H₆), δ : 22.26 (s). Found (%): N, 4.97; P, 5.51; Cl, 6.31. C₅₂H₄₄Cl₂N₄O₄P₂Pd₂. Calculated (%): N, 4.56; P, 5.29; Cl, 6.30.

trans-Chlorobis- (15a) and cis-chlorobis(triethylphosphine)(3-phenylsydnone-4-ylmercurio)platinum (15b). Pt(PPh₃)₄ (4.78 g, 3.84 mmol) was added to a suspension of 4-chloromercurio-3-phenylsydnone (1.53 g, 3.84 mmol) in 20 mL of benzene. The reaction mixture was stirred for 2 h at ~20 °C and filtered. The white crystalline product formed was washed with 50 mL of ether and dried *in vacuo* to give 3.35 g (78%) of a mixture of isomers **15a** and **15b**. ³¹P NMR (C₆H₆), δ : 12.56 (d, $J = 14.5$ Hz (dd, $J(^{195}\text{Pt}-^{31}\text{P}_\text{A}) = 2414.7$ Hz)); 13.93 (s, $J(^{195}\text{Pt}-^{31}\text{P}) = 3679.9$ Hz); 19.42 (d, $J = 14.5$ Hz (dd, $J(^{195}\text{Pt}-^{31}\text{P}_\text{B}) = 2996.4$ Hz)). Found (%): C, 47.31; H, 3.14; N, 4.97; P, 5.55. C₄₄H₃₅ClHgN₂O₂P₂Pt. Calculated (%): C, 47.05; H, 3.59; N, 4.56; P, 5.51.

trans-Chlorobis(triethylphosphine)(3-phenylsydnone-4-yl)platinum (16). A stirred solution of the mixture of **15a** and **15b** (2.35 g, 2.1 mmol) in 50 mL of benzene was exposed to UV radiation at ~20 °C for 3 h. The precipitated metallic mercury was separated and the white precipitate was filtered off, washed with 50 mL of ether, and dried *in vacuo* to give 0.69 g (36%) of compound **16**, m.p. 269–271 °C. ³¹P NMR (CDCl₃), δ : 12.11 (s, $J(^{195}\text{Pt}-^{31}\text{P}) = 3560$ Hz). Found (%): C, 57.67; H, 3.82; Cl, 6.77. C₄₄H₃₅ClN₂O₂P₂Pt. Calculated (%): C, 57.36; H, 3.76; Cl, 6.54.

trans-Bromobis(triethylphosphine)(3-phenylsydnone-4-ylcarbonyl)nickel (17). A flow of CO prepared by dehydration of formic acid was passed for 2 h at ~20 °C through a suspension of complex **3** (0.53 g, 1 mmol) in 30 mL of hexane. The resulting dark-yellow precipitate was filtered off, washed with pentane, and dried in an argon flow to give compound **17** in a yield of 0.042 g (75%). IR, ν/cm^{-1} : 1705, 1770. Found (%):

C, 44.02; H, 6.13; Br, 10.80. $C_{21}H_{35}BrN_2NiO_3P_2$. Calculated (%): C, 44.37; H, 6.15; Br, 10.55.

trans-Bromobis(triphenylphosphine)(3-phenylsydnnon-4-ylcarbonyl)palladium (18). A suspension of a mixture of **6a** and **6b** (0.87 g, 1 mmol) in 30 mL of THF was placed in an autoclave and stirred under a CO pressure of $25 \cdot 10^5$ Pa for 2 h at 50 °C. The CO pressure was reduced to atmospheric pressure and the temperature was decreased to ~20 °C. A sample for recording the spectrum was taken from the mixture. ^{31}P NMR, (THF), δ : 21.56 (s). IR, ν/cm^{-1} : 1700, 1770.

trans-Bromobis(triphenylphosphine)(3-phenylsydnnon-4-ylcarbonyl)platinum (19). A suspension of complex **7** (0.96 g, 1 mmol) in 30 mL of THF was placed in an autoclave and stirred under a CO pressure of $25 \cdot 10^5$ Pa for 2 h at 50 °C. Then the CO pressure was reduced to atmospheric pressure and the temperature was decreased to ~20 °C. A sample for recording the spectrum was taken from the mixture. ^{31}P NMR (THF), δ : 12.35 (s, $J(^{195}Pt-^{31}P) = 3567$ Hz). IR, ν/cm^{-1} : 1715, 1728, 1780.

References

1. J. K. Stille, in *The Chemistry of the Metal-Carbon Bond*, v. 2, Eds. F. R. Hartley and S. Patai, John Wiley and Sons Ltd., New York, 1985.
2. D. Mango, *Coord. Chem. Rev.*, 1975, **15**, 109.
3. K. Isobe, K. Nanjo, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2141.
4. B. Crociani, F. Di Bianca, A. Ciocovenco, A. Berton, and R. Bertani, *J. Organomet. Chem.*, 1989, **364**, 255.
5. A. Mantovani, *J. Organomet. Chem.*, 1983, **255**, 385.
6. V. V. Bashilov, E. B. Maskaeva, P. V. Petrovskii, V. I. Sokolov, and O. A. Reutov, *Metalloorgan. Khim.*, 1988, **1**, 61 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
7. O. Rossel, J. Sales, and M. Seco, *J. Organomet. Chem.*, 1982, **236**, 415.
8. L. S. Isaeva, L. N. Morozova, V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, and O. A. Reutov, *J. Organometal. Chem.*, 1983, **243**, 253.
9. E. V. Maskaeva, V. V. Bashilov, M. V. Galakhov, and V. I. Sokolov, *Metalloorgan. Khim.*, 1991, **4**, 910 [*Organomet. Chem.*, 1991, **4** (Engl. Transl.)].
10. V. V. Bashilov, V. I. Sokolov, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2069 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31** (Engl. Transl.)].
11. L. I. Zakharkin and I. V. Pisareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 252 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27** (Engl. Transl.)].
12. L. N. Morozova, L. S. Isaeva, P. V. Petrovskii, D. N. Kravtsov, F. M. She, and V. N. Kalinin, *J. Organomet. Chem.*, 1990, **381**, 281.
13. V. N. Kalinin, F. M. She, and P. V. Petrovskii, *J. Organomet. Chem.*, 1989, **379**, 195.
14. Urata, M. Tanaka, and T. Fuchigami, *Chem. Lett.*, 1987, 751.
15. D. Minniti, *Inorg. Chem.*, 1994, **33**, 2631.
16. L. Casado and P. Esprinet, *Organometallics*, 1998, **17**, 954.
17. M. Ohta and H. Kato, in *Nonbenzenoid Aromatics*, Ed. J. P. Snyder, Acad. Press, New York, 1969, 117.
18. V. I. Sokolov and O. A. Reutov, *Coord. Chem. Rev.*, 1978, **27**, 89.
19. G. Whlig and D. Walther, *Coord. Chem. Rev.*, 1980, **33**, 31.
20. D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, 1974, 2501.
21. S. P. Dent, C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organomet. Chem.*, 1972, **46**, C68.
22. D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.
23. J. K. Stille and A. B. Cowel, *J. Organomet. Chem.*, 1977, **124**, 253.
24. S. Cundy, *J. Organomet. Chem.*, 1974, **69**, 305.
25. R. Mynott, A. Mollbach, and G. Wilke, *J. Organomet. Chem.*, 1980, **199**, 107.
26. D. R. Coulson, L. C. Satek, and S. O. Grim, *Inorg. Synth.*, 1969, **13**, 121.
27. R. Ugo and F. Gariati, *Inorg. Synth.*, 1968, **11**, 1051.
28. K. Turnbull, *J. Het. Chem.*, 1985, **22**, 965.
29. K. Nakahara and M. Ohta, *Nippon Kagaku Zasshi*, 1956, **77**, 1306.

Received October 12, 2000