for Ir 5d, $\zeta_1 = 5.796, c_1 = 0.6698, \zeta_2 = 2.557, c_2 = 0.5860$;[46] for Mn 3d, $\zeta_1 = 5.15, c_1 = 0.51392, \zeta_2 = 1.70, c_2 = 0.6929$.[47] The d orbital H_{ii}'s were Mn −11.67 eV, Ir −12.17 eV.

In the model studies of comparative donor properties we used a pseudochlorine atom with its 3p H_{ii} shifted up or down by 2 eV to simulate a better or poorer donor.

[46] H. Basch and H. B. Gray, *Theor. Chim. Acta*, 4, 367 (1966).

[47] J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 36, 1057 (1962).

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Novel Rhodium and Palladium Complexes from Benzoyl and Thiobenzoyl Isocyanates

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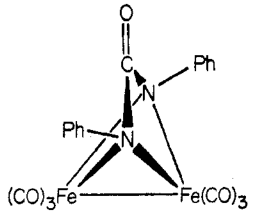
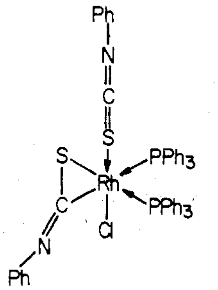
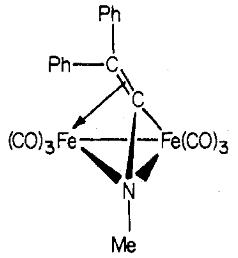
The reaction between benzoyl isocyanate and $\mathrm{RhCl(Ph_3P)_3}$ afforded a complex $\mathrm{[RhCl(Ph_3P)_2(PhCONCO)]_2}$ (**1**), which was converted to $\mathrm{[(bipy)Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-}$ (**2a**) by bipyridine and $\mathrm{NaBPh_4}$. The latter complex was also obtained by the reaction of $\mathrm{[(bipy)Rh(cyclooctadiene)]^+BPh_4^-}$, triphenylphosphine, and benzoyl isocyanate. An analogous palladium complex (bipy)Pd(PhCONCO) (**3**) was prepared in the reaction of $\mathrm{Pd_2(dibenzylideneacetone)_3}$ with bipyridine and benzoyl isocyanate. 2-Phenylthiazoline-4,5-dione (**4**), a precursor of thiobenzoyl isocyanate, gave $\mathrm{RhCl(CO)(Ph_3P)_2(PhCSNCO)}$ (**5**) in the reaction with either $\mathrm{RhCl(Ph_3P)_3}$ or $\mathrm{RhCl(CO)(Ph_3P)_2}$. A cationic complex $\mathrm{[(bipy)Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-}$ (**6a**) was also prepared from **4**. The similar reactions of $\mathrm{Pd_2(dibenzylideneacetone)_3}$ with **4** and bipyridine or *o*-phenanthroline afforded $(\overset{\frown}{\mathrm{N\ N}})$Pd(PhCSNCO) (**7**). Most of these novel complexes have a metallocyclic structure composed of M–O–C–N–C or M–S–C–N–C skeltons.

Introduction

No systematic investigations of the coordinating properties of benzoyl and thiobenzoyl isocyanates with low-valent transition metals have been reported, although some transition metal complexes of simple heterocumulene compounds were known.[1-5] Manuel originally reported $\mathrm{[(CO)_3Fe(PhNCO)]_2}$ in the reaction of phenyl isocyanate with $\mathrm{Fe_3(CO)_{12}}$;[1a] however, later structural investigations[1b-1d] concluded that the original complex was a diphenylurea complex of diiron hexacarbonyl. Similar types of urea complexes were isolated recently in the case of arylsulfonyl isocyanates.[1e] Baird and Wilkinson[2] prepared π- and S-bonded phenyl isothiocyanate complexes of nickel, palladium, platinum, rhodium, and iridium. The preparation and X-ray study of ketenimine complexes of iron were achieved by Otsuka.[3,4] Bycroft and Cotton[5] obtained carbodiimide-palladium(II) complexes with the formula $\mathrm{(RN{=}C{=}NR')_2PdX_2}$. The representative structures of some transition metal complexes induced from simple heterocumulene compounds are shown below.

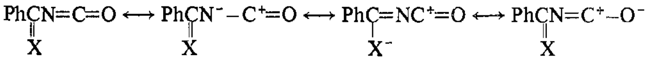






On the other hand, the five-membered metallocyclic complexes containing heteroatoms as the ring member have attracted much attention in recent years.[6-9] In particular, *N*-acylhydrazine or diazenes were found to be an excellent precursor to generate various five-membered metallocyclic systems (M-O-C-N-N), for instance, $\mathrm{[(PhCON{=}N)_2Cu]^+}$,[6] $\mathrm{MoCl_2(NAr)(ArCON{=}NAr)(PhMe_2P)}$,[7] $\mathrm{[(diphos)_2WCl(N{=}NCOR)]}$,[8] and $\mathrm{Pt(Ph_3P)_2(PhCON{=}NCOPh)}$.[9] The five-membered structure was definitely concluded by Ittel and Ibers[9] for the final complex by means of X-ray structural determination.

The following canonical structures (X = O or S) can be represented for (thio)benzoyl isocyanate and are corresponding to three possible modes of coordination.



$$\mathrm{Ph}\underset{\substack{\|\\ \mathrm{X}}}{\mathrm{C}}\mathrm{N{=}C{=}O} \longleftrightarrow \underset{a}{\mathrm{Ph}\underset{\substack{\|\\ \mathrm{X}}}{\mathrm{C}}\mathrm{N^-{-}C^+{=}O}} \longleftrightarrow \underset{b}{\mathrm{Ph}\underset{\substack{|\\ \mathrm{X^-}}}{\mathrm{C}}\mathrm{{=}NC^+{=}O}} \longleftrightarrow \underset{c}{\mathrm{Ph}\underset{\substack{\|\\ \mathrm{X}}}{\mathrm{C}}\mathrm{N{=}C^+{-}O^-}}$$

Our studies on the addition-elimination reactions of benzoyl and thiobenzoyl isocyanates with group IVb organometallic compounds disclosed a lot of interesting results indicative of the occurrence of the 1,4 addition of these hetero-

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(1) (a) T. A. Manuel, *Inorg. Chem.*, 3, 1703 (1964); (b) J. A. J. Jarvis, B. E. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Commun.*, 1149 (1967); (c) J. Piron, P. Piret, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, 76, 505 (1967); (d) W. T. Flannigan, G. R. Knox, and P. L. Pauson, *Chem. Ind. (London)*, 1094 (1967); (e) W. Beck, W. Hieber, S. Cenini, F. Porta, and G. LaMonica, *J. Chem. Soc., Dalton Trans.*, 298 (1974).

(2) M. C. Baird, G. Hartwell, and G. Wilkinson, *J. Chem. Soc. A*, 865, 2037 (1967).

(3) S. Otsuka, A. Nakamura, and T. Yoshida, *J. Organometal. Chem.*, 7, 339 (1967).

(4) K. Ogawa, A. Torii, H. Kobayashi-Tamura, T. Watanabe, T. Yoshida, and S. Otsuka, *Chem. Commun.*, 991 (1971).

(5) B. M. Bycroft and J. D. Cotton, *J. Chem. Soc., Dalton Trans.*, 1867 (1973).

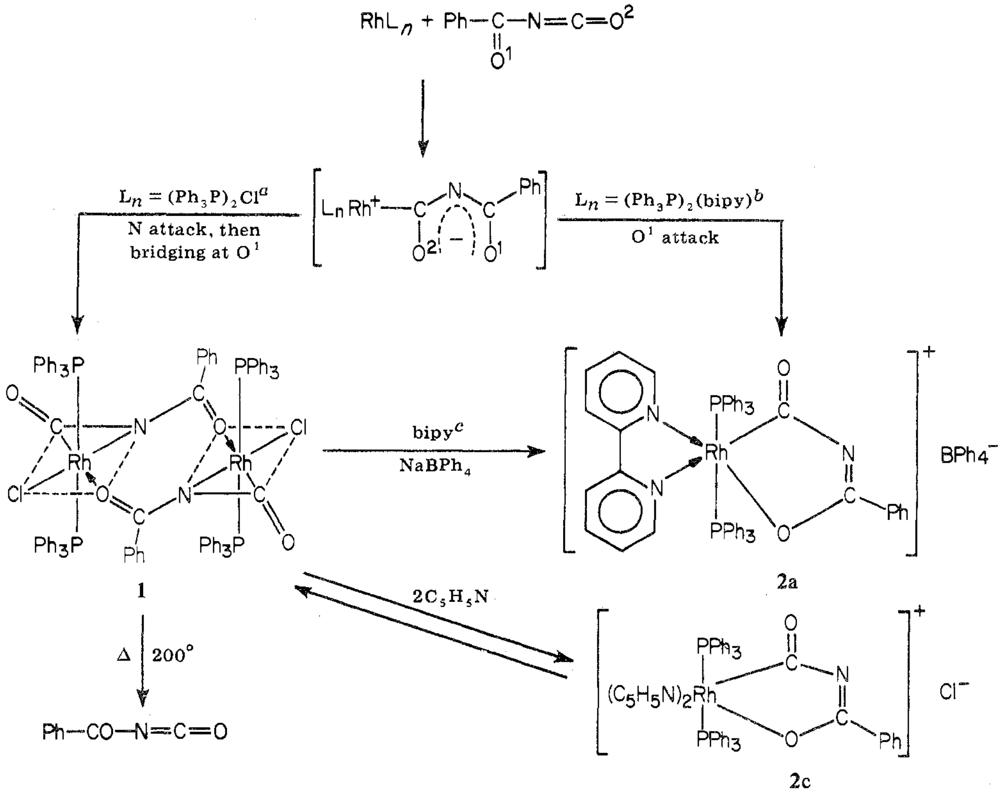
(6) R. J. Baker, S. C. Nyburg, and J. T. Szymanski, *Inorg. Chem.*, 10, 138 (1971).

(7) J. Chatt and J. D. Dilworth, *J. Chem. Soc., Chem. Commun.*, 549 (1972).

(8) J. Chatt, G. A. Heath, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 444 (1972).

(9) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, 12, 2290 (1973).

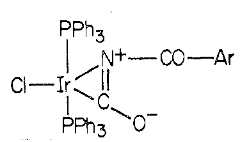
Scheme I

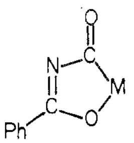


^{a} Rh(Ph$_3$P)$_3$Cl − Ph$_3$P. ^{b} [(bipy)Rh(cyclooctadiene)]$^+$ + 2Ph$_3$P − cyclooctadiene. ^{c} When *o*-phenanthroline was used instead of bipyridine, [(*o*-phen)Rh(PhCONCO)]$^+$BPh$_4^-$ (2b) was obtained.

cumulene systems (mode b),[10] which had stimulated us to investigate the interaction of these heterocumulene systems with low-valent transition metals.

In this context, Collman, *et al.*,[11] obtained IrCl(Ph$_3$P)$_2$(ArCONCO) in the reaction between Vaska's complex and aroyl azide and proposed the following structure in which nitrogen and carbonyl carbon atoms of the isocyanate group coordinated to the iridium atom (mode a). Another probability, the 1,4 addition of (thio)benzoyl isocyanate by mode b, should induce a new five-membered metallocyclic complex containing two heteroatoms (N and O or S).





In this paper, the results of reactions between benzoyl or thiobenzoyl isocyanate and various rhodium(I) or palladium(0) complexes are described.

Results and Discussion

Reactions of Benzoyl Isocyanate with Rhodium(I) Complexes. The reaction of tris(triphenylphosphine)chlororhodium, RhCl(Ph$_3$P)$_3$, with excess of benzoyl isocyanate[12] in benzene at room temperature under nitrogen gave yellow needlelike crystals of [RhCl(Ph$_3$P)$_2$(PhCONCO)]$_2$ (1) in 89% yield. From large lower frequency shifts of infrared absorptions, ν(NCO) 1710 and ν(CO) of benzoyl group 1400 cm^{-1} (absorptions of the free ligand were 2240 and 1690 cm^{-1}, respectively), both of the isocyanate and the benzoyl carbonyl groups of benzoyl isocyanate may coordinate to rhodium atom, just like the ketenimine group coordination to cobalt in the case of π-C$_5$H$_5$Co(Ph$_2$C=C=NMe)[3] (with a change of ν(CCN) from 1998 to 1565 cm^{-1} on coordination). Complex 1 is very stable in air and in solvent. When 1 was heated up to 200° under reduced pressure, benzoyl isocyanate was recovered quantitatively.

Evidence for the structure of 1 was supplemented by the following reaction. When excesses of sodium tetraphenylborate and bipyridine (bipy) were added to 1 in CH$_2$Cl$_2$-CH$_3$OH at room temperature, pale yellow platelike crystals of [(bipy)Rh(Ph$_3$P)$_2$(PhCONCO)]$^+$BPh$_4^-$ (2a) were isolated in 72% yield. The ν(CO) absorption of 2a (1623 cm^{-1}) implies the acyl-type bonding with rhodium metal as a five-membered ring structure: Rh–O–C=N–C as depicted in Scheme I. The conversion from 1 to 2a could be followed by recording the infrared spectrum of the reaction mixture at different times (Figure 1). As shown in Figure 1, ν(CO) of 1 at 1710 cm^{-1} began to disappear gradually, in accordance with the increase of ν(CO) of 2a at 1623 cm^{-1}, which means that bipyridine displaces the bridging oxygen atom and the nitrogen atom of 1, followed by the bond formation between Rh metal and benzoyl oxygen with simultaneous liberation of chloride anion which was trapped by sodium cation, to yield the more stable 1,4-metallocyclic complex (2a).

The cationic complex (2a) could be prepared independently by the reaction of [(bipy)Rh(cyclooctadiene)]$^+$BPh$_4^-$[13] with benzoyl isocyanate under excess of triphenylphosphine in refluxing CH$_2$Cl$_2$ in lower yield (34%).

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(10) I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc. C*, 701 (1969); 1870 (1971); *Tetrahedron Lett.*, 2675 (1969); *J. Organometal. Chem.*, 19, 339, 347 (1969); *J. Chem. Soc., Perkin Trans.*, 1, 1678 (1972).

(11) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, 90, 5430 (1968).

(12) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, 27, 3742 (1962).

(13) C. Cocevar, G. Mestroni, and A. Camus, *J. Organometal. Chem.*, 35, 389 (1972).

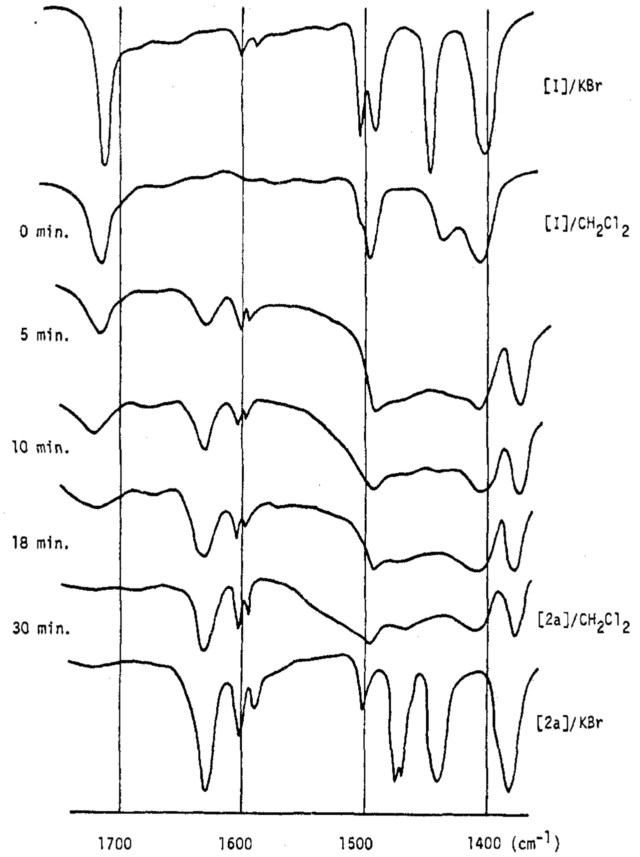
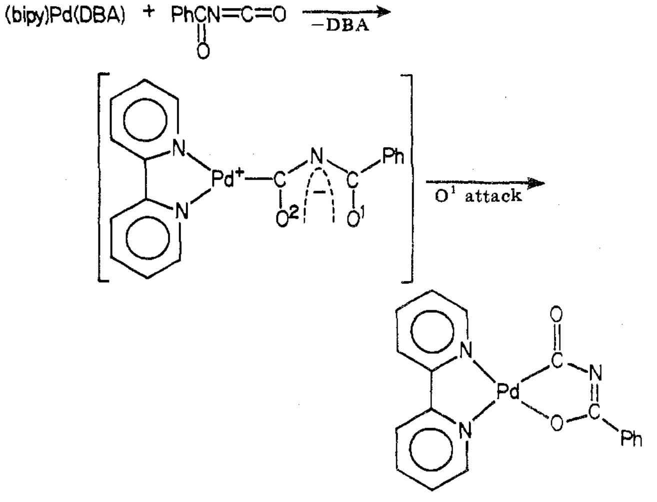


Figure 1. Variation of infrared spectrum with time for the conversion from $[RhCl(Ph_3P)_2(PhCONCO)]_2$ (1) to $[(bipy)Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (2a) by bipyridine and sodium tetraphenylborate in CH_2Cl_2-CH_3OH.

An analogous cationic complex (**2b**) which involves *o*-phenanthroline (*o*-phen) as a stabilizing ligand instead of bipy was obtained in 73% yield from **1**, *o*-phen, and sodium tetraphenylborate (ν(CO) 1628 and 1379 cm^{-1}). In contrast to the reaction with bipy or *o*-phen, the reaction between **1** and pyridine in CH_2Cl_2 produced a reversible change to $[(py)_2Rh(PPh_3)_2(PhCONCO)]^+Cl^-$ (ν(CO) at 1625 cm^{-1}) (**2c**) instantaneously, which returned to **1** on recrystallization from CH_2Cl_2-$(C_2H_5)_2O$.

These reactions were summarized in Scheme I. The nucleophilic attack of rhodium(I) complexes on the carbon atom of the isocyanate group may be the primary step, followed by N, O^1 attack (more precisely, at first N attack and the following O^1 bridging to dimerization) in the case of $RhCl(PPh_3)_3$ or by O^1 attack on the $[(bipy)Rh(PPh_3)_2]^+$ species. Due to dissociation of one molecule of triphenylphosphine from $RhCl(PPh_3)_3$, the resulting coordinatively unsaturated $RhCl(PPh_3)_2$ may accept benzoyl isocyanate as a tridentate ligand (C, N, and O^1) [modes a and b] to complete six-coordination around Rh(III), while $[(bipy)Rh(PPh_3)_2]$ has a coordination number of 4 and benzoyl isocyanate behaves as a bidentate ligand (C and O^1) [mode b]. Because the metal basicity of $Rh(CO)(Ph_3P)_2Cl$ or $Rh^+(Ph_3P)_2$(cyclooctadiene) is lower than that of $RhCl(Ph_3P)_3$ or $Rh^+(Ph_3P)_2$(bipy), the former did not react with benzoyl isocyanate. The determination of the X-ray structures of **1** and **2a** is in progress by Professor J. A. Ibers at Northwestern University.

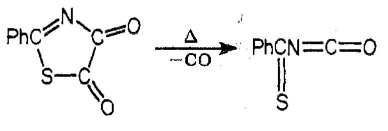
Reactions of Benzoyl Isocyanate with Tris(dibenzylideneacetone)dipalladium. Tris(dibenzylideneacetone)dipalladium, $Pd_2(DBA)_3$, was found as a useful complex in oxidative addition reactions, ligand-exchange reactions, and preparation of (*p*-quinone)PdL_2 and palladiacyclopentadiene complexes.[14,15] When an excess of bipyridine was added to an ether solution of $Pd_2(DBA)_3$ and benzoyl isocyanate under nitrogen at room temperature, orange crystals of (bipy)Pd(PhCONCO)·$^1/_2CH_2Cl_2$ (**3**) was obtained in 75% yield after recrystallization from methylene chloride. In this case, benzoyl isocyanate acts as a bidentate ligand (C and O^1) to form stable 1,4 coordination of benzoyl isocyanate to square-planar palladium (mode b; ν(CO) 1630 cm^{-1}).



3

No stable complex was obtained when an excess of triphenylphosphine was used instead of bipyridine in the above-mentioned reaction.

Reactions of 2-Phenylthiazoline-4,5-dione with Rh(I) Complexes. 2-Phenylthiazoline-4,5-dione (**4**) is a precursor of thiobenzoyl isocyanate which was generated by heating **4** in refluxing methylcyclohexane.[16]



4

In the reaction between $RhCl(Ph_3P)_3$ and an excess of **4** in benzene at room temperature under nitrogen, a precipitate of yellow crystals of $RhCl(CO)(Ph_3P)_2(PhCSNCO)$ (**5**) was obtained in 50% yield. The infrared spectrum of **5** shows the acyl carbonyl absorption at 1623 and an Rh-CO band at 2070 cm^{-1}.

The same complex **5** could also be prepared in 64% yield in the reaction of **4** with $RhCl(CO)(Ph_3P)_2$ in refluxing toluene with the evolution of carbon monoxide. On heating **5** in refluxing chloroform, decomposition to thiobenzoyl isocyanate and $RhCl(CO)(Ph_3P)_2$ was observed.

On the other hand, the reaction of **4** with $[(bipy)Rh(COD)]^+BPh_4^-$ or $[(o\text{-phen})Rh(COD)]^+BPh_4^-$ in the presence of excess triphenylphosphine in refluxing mixed solvent (CH_2Cl_2:toluene = 1:2) for 6 hr gave yellow needlelike crystals of $[(bipy)Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (**6a**; 69% yield) or yellowish prismlike crystals of $[(o\text{-phen})Rh(Ph_3P)_2(Ph$-

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(14) (a) Y. Takahashi, Ts. Ito, S. Sakai, and Y. Ishii, *Chem. Commun.*, 1065 (1970); (b) Ts. Ito, S. Hasegawa, Y. Takahashi, and Y. Ishii, *ibid.*, 629 (1972); (c) T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organometal. Chem.*, 65, 253 (1974).

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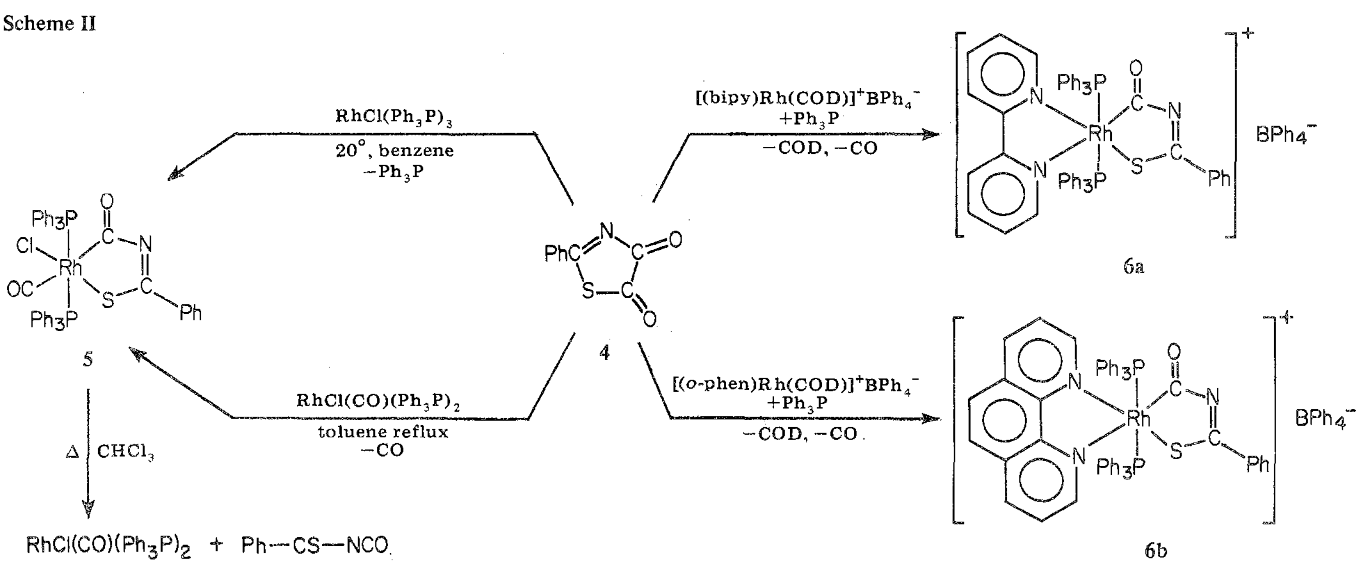
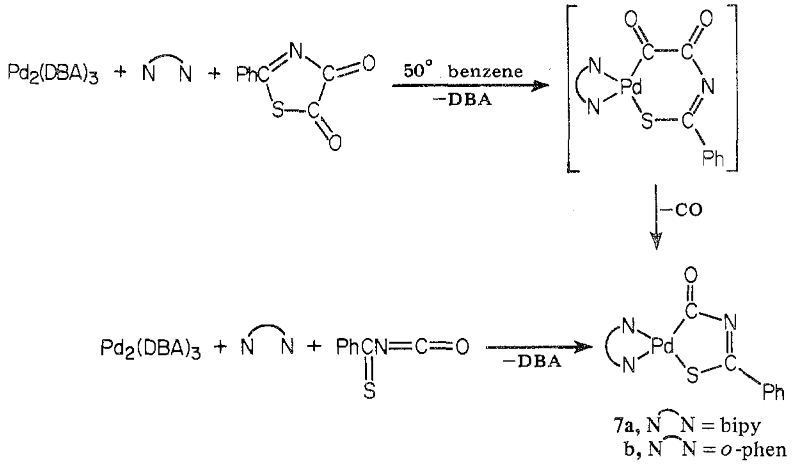
(16) J. Goerdeler and H. Schenk, *Chem. Ber.*, 98, 2954 (1965).

Scheme II



Scheme III



CSNCO)]$^+$BPh$_4^-$ (**6b**; 85% yield), respectively. Their structures were identified by analysis and the ν(CO) absorption bands (**6a**, 1620 cm^{-1}; **6b**, 1615 cm^{-1}) indicative of a five-membered metallocyclic structure (mode b).

These results are summarized in Scheme II.

Reactions of 2-Phenylthiazoline-4,5-dione with Tris(dibenzylideneacetone)dipalladium. When the benzene solution of Pd$_2$(DBA)$_3$ with an excess of bipyridine and **4** was heated to 50°, evolution of carbon monoxide occurred violently. The product was reddish needlelike crystals of (bipy)-Pd(PhCSNCO) (**7a**) in 92% yield. The same complex **7a** was also obtained in 63% yield in the reaction of Pd$_2$(DBA)$_3$ with thiobenzoyl isocyanate, generated *in situ* from **4**, in the presence of bipyridine. When *o*-phenanthroline was used instead of bipyridine in the reaction of **4** with Pd$_2$(DBA)$_3$, (*o*-phen)Pd(PhCSNCO) (**7b**) was obtained in 84% yield.

However, when biacetyldianil was used in the analogous reaction, no evolution of carbon monoxide was observed. The sole product was brownish needlelike crystals of the complex with the composition of [(PhN=CMe–MeC=NPh)Pd-(C$_9$H$_5$NO$_2$S)] (**8**) in 76% yield. In the infrared spectrum, a broad absorption band at 1660 cm^{-1} is quite different from those of either **7a** or **7b**. Consequently, **8** may correspond to the unidentified reaction intermediate shown in brackets in Scheme III. Complex **8** did not evolve carbon monoxide upon heating, only causing decomposition to metallic palladium.

Experimental Section

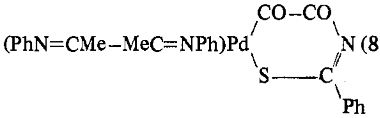
General Remarks. All reactions were performed under an atmosphere of nitrogen. Infrared spectra were measured by means of a Japan Spectroscopic Co. Model DS-403G spectrometer as a KBr disk unless otherwise described. Benzoyl isocyanate[12] and 2-phenylthiazoline-4,5-dione[15] were prepared according to the references.

[RhCl(Ph$_3$P)$_2$(PhCONCO)]$_2$ (1). To a benzene (20 ml) solution of chlororhodium tris(triphenylphosphine), RhCl(Ph$_3$P)$_3$ (870 mg, 0.94 mmol), an excess of benzoyl isocyanate (410 mg, 2.50 mmol) was added with stirring. The color of the solution changed gradually from deep red to yellow, and a yellow crystalline product started to precipitate in 1 hr. The mixture was stirred for 6 hr at room temperature. Then a yellow precipitate of bis(μ-(benzoyl isocyanate))-dichlorotetrakis(triphenylphosphine)dirhodium, [RhCl(Ph$_3$P)$_2$(PhCO-NCO)]$_2$ (**1**), was isolated by filtration and followed by recrystallization from methylene chloride–ethyl ether mixed solvent as yellow needles (638 mg, 89%). Melting points, analytical results, and ν(C=O) bands of products including **1** are summarized in Table I.

[(bipy)Rh(Ph$_3$P)$_2$(PhCONCO)]$^+$BPh$_4^-$ (2a). Method A. Sodium tetraphenylborate (120 mg, 0.35 mmol) and bipyridine (90 mg, 0.58 mmol) were added to **1** (210 mg, 0.13 mmol) dissolved in 20 ml of methylene chloride–methanol (3:1 volume ratio) mixed solvent. The mixture was kept stirring for 24 hr, and the starting yellow solution changed to a pale yellow solution and suspended white precipitate of sodium chloride. After the reaction, sodium chloride was removed by filtration and was washed with methylene chloride. Methanol was added to the filtrate and washings, and the solution was kept in a refrigerator overnight. Pale yellow plates of [(bipy)Rh(Ph$_3$P)$_2$(Ph-CONCO)]$^+$BPh$_4^-$ (**2a**) were isolated by filtration in 72% yield (226 mg).

Method B. A mixture of triphenylphosphine (438 mg, 1.57 mmol), benzoyl isocyanate (0.5 ml), and [(bipy)Rh(1,5-cycloocta-

Table I. Analytical Results for Benzoyl or Thiobenzoyl Isocyanate Complexes of Rhodium and Palladium

Complex	Yield %	Mp, °C	Color	Analysis, % C Calcd	Analysis, % C Found	Analysis, % H Calcd	Analysis, % H Found	Analysis, % N Calcd	Analysis, % N Found	Ir-(KBr), ν(C=O), cm^{-1}
$[RhCl(Ph_3P)_2(PhCONCO)]_2$ (1)	89	206–208 dec	Yellow	65.24	65.18	4.36	4.24	1.73	1.76	1710
$[(bipy)Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (2a)	72	187–188	Pale yellow	74.95	74.64	5.08	5.25	3.36	3.50	1623
$[(o\text{-phen})Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (2b)	71	212–214 dec	Pale yellow	75.45	75.55	4.99	5.25	3.38	3.18	1628
$(bipy)Pd(PhCO{\cdot}NCO){\cdot}{}^1/_2CH_2Cl_2$ (3)	75	202–207 dec	Orange	49.14	48.36	3.24	3.12	9.29	9.34	1630
$RhCl(CO)(Ph_3P)_2(PhCSNCO)$ (5)	50	210–212 dec	Yellow	63.28	63.41	4.13	4.11	1.64	1.62	1623
$[(bipy)Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (6a)	69	197–199 dec	Yellow	74.00	73.82	5.02	5.08	3.32	3.21	1620
$[(o\text{-phen})Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (6b)	85	217–219 dec	Yellow	74.48	74.24	4.92	4.88	3.26	3.32	1615
(bipy)Pd(PhCSNCO) (7a)	63	185–190 dec	Red	50.78	50.44	3.08	3.20	9.87	9.79	1620
(*o*-phen)Pd(PhCSNCO) (7b)	84	200–205 dec	Red	53.41	53.59	2.91	2.81	9.34	9.31	1630
 (8)	76	159–163 dec	Brown	56.24	55.77	3.96	4.19	7.87	8.05	1660

diene)]$^+BPh_4^-$ (380 mg, 0.55 mmol)[13] in methylene chloride (20 ml) was refluxed for 10 hr. The starting red color of the homogeneous solution changed gradually to yellow. The reaction mixture was allowed to stand overnight to crystallize out **2a**, which was isolated and recrystallized from methylene chloride–methanol mixed solvent in 34% yield (210 mg). Complex **2a** showed a melting point and infrared spectrum indentical with those of **2a** prepared according to method A.

$[(o\text{-phen})Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (2b). In a similar procedure, **2b** was prepared in 71% yield by the reaction of **1** (210 mg, 0.13 mmol) with *o*-phenanthroline (176 mg, 0.98 mmol) in the presence of sodium tetraphenylborate (342 mg, 0.42 mmol).

Reversible Formation of $[(C_5H_5N)_2Rh(PhCONCO)]^+Cl^-$ (2c) from 1. The addition of pyridine (0.1 ml) to a methylene chloride solution (20 ml) of **1** (230 mg, 0.14 mmol) caused the color to change to yellow. An infrared spectrum showed a strong absorption at 1625 cm^{-1} due to ν(CO), indicative of the formation of **2c**. Removal of solvent under reduced pressure followed by recrystallization from methylene chloride–methanol returned to the original complex (**1**), which showed the same melting point and ir spectrum as the authentic sample.

(bipy)Pd(PhCONCO) (3). Bipyridine (526 mg, 3.30 mmol) and benzoyl isocyanate (0.5 ml) were added to an ether (20 ml) suspension of tris(dibenzylideneacetone)dipalladium, $Pd_2(DBA)_3$ (500 mg, 0.55 mmol), at room temperature. After 5 hr the dark red crystals had disappeared and orange crystals appeared, which were collected by filtration and were recrystallized from CH_2Cl_2–Et_2O mixed solvent to give yellow needle crystals of **3** as a half-solvate of methylene chloride. They were dried under vacuum to give orange crystals of $(bipy)Pd(PhCONCO){\cdot}{}^1/_2CH_2Cl_2$ (**3**) in 75% yield (340 mg). The presence of methylene chloride as solvate was confirmed by an nmr spectrum and analyses.

$[RhCl(CO)(Ph_3P)_2(PhCSNCO)]$ (5). Method A. The benzene solution (20 ml) of $RhCl(Ph_3P)_3$ (200 mg, 0.33 mmol) was added to 2-phenylthiazoline-4,5-dione (**4**) (100 mg, 0.52 mmol) at room temperature with stirring. The red color of the solution turned gradually to yellow. Yellow crystals of **5** precipitated and were isolated by filtration followed by washing with methylene chloride in 50% yield (95 mg); ν(C≡O) 2070 and ν(C=O) 1625 cm^{-1}.

Method B. A toluene solution (20 ml) of $RhCl(CO)(Ph_3P)_2$ (270 mg, 0.41 mmol) and **4** (110 mg, 0.57 mmol) was refluxed until evolution of carbon monoxide ceased. After filtration $RhCl(CO)(Ph_3P)_2$-(PhCSNCO) (**5**) was obtained in 64% yield (220 mg) and identified by ir spectrum, melting point, and analysis.

When the chloroform suspension of **5** was refluxed, dissociation of thiobenzoyl isocyanate was observed with the formation of RhCl-$(CO)(Ph_3P)_2$.

$[(bipy)Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (6a). A mixture of [(bipy)-Rh(COD)]$^+BPh_4^-$ (200 mg, 0.29 mmol) in 20 ml of the mixed solvent CH_2Cl_2-toluene (1:2 volume ratio) was stirred for 6 hr with triphenylphosphine (180 mg, 0.69 mmol) and **4** (80 mg, 0.42 mmol). Yellow crystals of **6a** precipitated and were isolated by filtration; recrystallization was achieved from CH_2Cl_2–MeOH in 69% yield as yellow prisms.

$[(o\text{-phen})Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (6b). In a manner similar to the preparation of **6a**, **6b** was prepared by the reaction of [(*o*-phen)Rh(COD)]$^+BPh_4^-$ (366 mg, 0.51 mmol) with triphenylphosphine (370 mg, 1.00 mmol) and **4** (130 mg, 0.68 mmol) in 85% yield.

(bipy)Pd(PhCSNCO) (7a). Method A. A mixture of $Pd_2(DBA)_3$ (200 mg, 0.22 mmol), bipyridine (200 mg, 1.4 mmol), and **4** (100 mg, 0.53 mmol) was stirred in benzene (20 ml) at 50°. Reaction took place gradually and the purple-red color of the solution changed to orange with the evolution of carbon monoxide, which stopped in 1 hr. Then the product was isolated as red crystals by filtration and was recrystallized from CH_2Cl_2–Et_2O in 92% yield (170 mg).

Method B. Complex **7a** was also prepared by reaction of PhCSNCO [generated *in situ* from **4** (265 mg, 1.38 mmol) in 10 ml of methylcyclohexane[16]] with $Pd_2(DBA)_3$ (403 mg, 0.44 mmol) and bipyridine (241 mg, 1.55 mmol) in 63% yield.

(*o*-phen)Pd(PhCSNCO) (7b). In a similar manner to the above procedure, **7b** was prepared by the reaction of $Pd_2(DBA)_3$ (200 mg, 0.22 mmol) with *o*-phenanthroline (230 mg, 1.28 mmol) and **4** (80 mg, 0.44 mmol) in 84% yield (159 mg).

$(PhN{=}CMe{-}MeC{=}NPh)Pd(C_9H_5NO_2S)$ (8). When $Pd_2(DBA)_3$ (303 mg, 0.31 mmol), biacetyldianil, PhN=CMe–MeC=NPh (213 mg, 0.96 mmol), and **4** (103 mg, 0.69 mmol) were mixed and stirred at room temperature, no gas evolution occurred but formation of a brown solid was observed. The product obtained by filtration was consistent with the composition of $(PhN{=}CMe{-}MeC{=}NPh)Pd(C_9H_5NO_2S)$ (**8**) by analysis, indicative of no loss of carbon monoxide from **4**.

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Registry No. **1**, 52483-62-2; **2a**, 52393-28-9; **2b**, 52393-30-3; **2c**, 52393-31-4; **3**, 52393-32-5; **5**, 52393-33-6; **6a**, 52393-35-8; **6b**, 52483-64-4; **7a**, 52393-36-9; **7b**, 52483-65-5; **8**, 52393-37-0; tris(triphenylphosphine)chlororhodium, 14694-95-2; [(bipy)Rh(1,5-cyclooctadiene)]$^+BPh_4^-$, 37685-02-2; [(*o*-phen)Rh(CoD)]$^+BPh_4^-$, 52513-61-8; tris(dibenzylideneacetone)dipalladium, 52409-22-0; bis(triphenylphosphine)carbonylchlororhodium, 13938-94-8; triphenylphosphine, 603-35-0; benzoyl isocyanate, 4461-33-0; bipyridine, 366-18-7; pyridine, 110-86-1; 2-phenylthiazoline-4,5-dione, 1628-53-1.