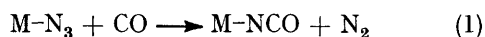


Carbonylation of Azido(thiocarbonyl) Complexes of Rhodium and Iridium

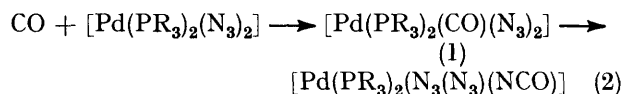
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The reactions of CO with *trans*-[M(PPh₃)₂(CS)(N₃)] (M = Ir or Rh) in benzene or chloroform solution result in the formation of *trans*-[M(PPh₃)₂(CO)(NCS)] rather than *trans*-[M(PPh₃)₂(CS)(NCO)]. Paths for the reactions including atom transfer in a five-co-ordinate intermediate and nucleophilic attack of co-ordinated CS by azide ion are discussed.

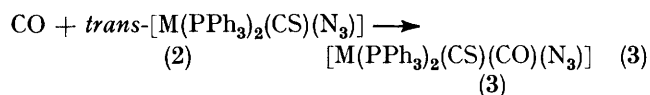
THE reactions of carbon monoxide with a variety of azido-transition-metal complexes including [M(PPh₃)₂(N₃)₂] (M = Pt or Pd), [M(PPh₃)₂(CO)(N₃)] (M = Rh or Ir), [Rh(PPh₃)₃(N₃)], [Au(PPh₃)₃(N₃)], and [Pd(N₃)₄]²⁻ give isocyanato-metal complexes.¹⁻³ Azido-complexes of



Cu and Ag do not give isocyanato-complexes with CO. The reaction of potassium azide and carbon monoxide to give potassium cyanate in aqueous solution is catalyzed by Pd on charcoal.² Kinetic studies of the reactions of CO with [Pd(PR₃)₂(N₃)₂] led to the suggestion of a mechanism in which a five-co-ordinate intermediate (1) is formed, followed by elimination of dinitrogen and migration of the nitrogen atom to CO.¹



It was of interest to study the carbonylation of the azido(thiocarbonyl) complexes (2; M = Ir or Rh) to determine whether the nitrogen-atom rearrangement in the five-co-ordinate intermediate (3) will give isocyanato-complexes (M-NCO) as mentioned above, or isothiocyanato-complexes (M-NCS).



EXPERIMENTAL

All the solvents were reagent grade materials which were degassed with nitrogen before use. Standard Schlenk techniques were used to handle all the iridium complexes in a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. The complexes *trans*-[Ir(PPh₃)₂(CS)Cl],⁴ *trans*-[Rh(PPh₃)₂(CS)Cl],⁵ [Ir(PPh₃)₂(CS)(CO)₂][ClO₄],⁶ *trans*-[Rh(PPh₃)₂(CO)(NCO)],² and *trans*-[Ir(PPh₃)₂(CO)(NCO)]² were synthesized using methods previously described (Found: C, 64.95; H, 4.40; N, 1.95. Calc. for C₃₈H₃₀NO₂P₂Rh: C, 65.45; H, 4.35; N, 2.00. Found: C, 58.05; H, 3.95; N, 1.75; P, 7.80. Calc. for C₃₈H₃₀IrNO₂P₂: C, 58.0; H, 3.85; N, 1.80; P, 7.85%).

Infrared-spectral Studies.—Carbon monoxide was bubbled into solutions of *trans*-[M(PPh₃)₂(CS)(N₃)] (M = Rh or Ir) (10 mg) in chloroform (2 cm³) and the spectra of the solutions were scanned in the 1 200—2 300 cm⁻¹ region within 2 min of introduction of the CO. The spectra indicated rapid

disappearance of the i.r. bands at 1 300 and 1 325 cm⁻¹ due to the thiocarbonyl complexes and formation of *trans*-[M(PPh₃)₂(CO)(NCS)]. Similar spectral studies conducted on the reactions of CO with [Pt(PPh₃)₂(N₃)₂] and [M(PPh₃)₂(CO)(N₃)] (M = Rh or Ir) indicated a slower rate of disappearance of the azido-complexes [ν(N₃) at 2 080 cm⁻¹] and slower growth of the band at 2 240 cm⁻¹ due to the isocyanato-complexes.

***trans*-Azido(thiocarbonyl)bis(triphenylphosphine)-rhodium(I).**—A mixture of *trans*-[Rh(PPh₃)₂(CS)Cl] (192 mg), Na[N₃] (400 mg), and PPh₃ (250 mg) in dichloromethane (20 cm³) and methanol (20 cm³) was heated under reflux for 2 h. The solvent was removed *in vacuo* and the yellow solid was washed successively with Et₂O (10 cm³), water (10 cm³), and MeOH (10 cm³). The yellow product was recrystallized from CH₂Cl₂ (5 cm³) and Et₂O (10 cm³), yield 90%, m.p. 175 °C (decomp.) (Found: C, 62.4; H, 4.40; N, 5.75. Calc. for C₃₇H₃₀N₃P₂RhS: C, 62.3; H, 4.25; N, 5.90%).

***trans*-Azido(thiocarbonyl)bis(triphenylphosphine)iridium(I).**—A mixture of *trans*-[Ir(PPh₃)₂(CS)Cl] (464 mg), Na[N₃] (504 mg), and PPh₃ (200 mg) in benzene (40 cm³) and methanol (40 cm³) was heated under reflux under nitrogen for 2.5 h. The solvent was removed *in vacuo*, and the solid was washed with water, ethanol, and Et₂O. The yellow solid was recrystallized from chloroform-methanol, yield 364 mg (78%) (Found: C, 54.95; H, 3.95; N, 6.20. Calc. for C₃₇H₃₀IrN₃P₂S: C, 55.35; H, 3.75; N, 5.25%).

***trans*-Carbonyl(isothiocyanato)bis(triphenylphosphine)-rhodium(I).**—A solution of *trans*-[Rh(PPh₃)₂(CS)(N₃)] (80 mg) in benzene (20 cm³) was treated with 20 lbf in⁻² † CO in a Fisher-Porter pressure bottle for 16 h. The yellow solution turned pale yellow. The solvent was removed *in vacuo* and the yellow product was recrystallized from dichloromethane (5 cm³) and methanol (10 cm³), yield 90%, m.p. 170—171 °C (decomp.) (Found: C, 64.15; H, 4.30; N, 2.05. Calc. for C₃₈H₃₀NOP₂RhS: C, 63.95; H, 4.25; N, 1.95%). This complex has been previously prepared by metathetical displacement of Cl in *trans*-[Rh(PPh₃)₂(CO)Cl].⁷

***trans*-Carbonyl(isothiocyanato)bis(triphenylphosphine)-iridium(I).**—A solution of *trans*-[Ir(PPh₃)₂(CS)(N₃)] (138 mg) in chloroform (20 cm³) was treated with CO at 1 atm pressure for 15 min. The solvent was removed *in vacuo* and the yellow product was recrystallized from chloroform-methanol. The product was dried *in vacuo* at 58 °C for 3 h, yield 109 mg (79%), m.p. 198—204 °C (decomp.) (Found: C, 57.1; H, 3.90; N, 1.55. Calc. for C₃₈H₃₀IrNOP₂S: C, 56.85; H, 3.75; N, 1.75%).

Carbonylation of *trans*-[Ir(PPh₃)₂(CO)(NCS)].—Carbon monoxide was bubbled into a solution of *trans*-[Ir(PPh₃)₂(CO)(NCS)] (10 mg) in chloroform (2 cm³) and the spectra of the solutions were scanned in the 1 200—2 300 cm⁻¹ region within 2 min of introduction of the CO. The spectra indicated rapid

† Throughout this paper: 1 lbf in⁻² ≈ (9.8 × 4 536)/6.45 Pa; 1 atm = 101 325 Pa.

(CO)(NCS)] (10 mg) in dichloromethane (5 cm³) until the solvent was completely evaporated. The yellow product was washed with Et₂O (5 cm³) and dried in a stream of nitrogen. The product [Ir(PPh₃)₂(CO)₂(NCS)] has bands at 2 085, 1 971, 1 945, and 850 cm⁻¹. Drying the product *in vacuo* for 2 h gave [Ir(PPh₃)₂(CO)(NCS)].

trans-Isocyanato(thiocarbonyl)bis(triphenylphosphine)-rhodium(I).—A mixture of *trans*-[Rh(PPh₃)₂(CS)Cl] (415 mg), Na[NCO] (509 mg), and PPh₃ (258 mg) in MeOH (40 cm³) and PhH (40 cm³) was heated under reflux under nitrogen for 4.5 h. The solvent was removed *in vacuo*, and the yellow solid was washed successively with EtOH (10 cm³), water (5 cm³), EtOH (5 cm³), and Et₂O (10 cm³). The product was recrystallized as yellow crystals (90%) from CHCl₃-EtOH (Found: C, 63.8; H, 4.25; N, 1.85. Calc. for C₃₈H₃₀NOP₂RhS: C, 63.95; H, 4.25; N, 1.95).

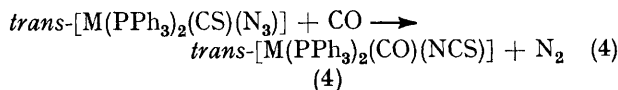
Reaction of [Ir(PPh₃)₂(CS)(CO)₂][ClO₄] with Sodium Azide.—A solution of Na[N₃] (10.4 mg) in water (2 cm³) was added to [Ir(PPh₃)₂(CS)(CO)₂][ClO₄] (55.9 mg) in acetone (5 cm³). There was immediate N₂ evolution and the mixture was stirred for 15 min. The acetone was removed under reduced pressure, and the pale yellow product was filtered off, washed with MeOH (2 × 3 cm³), and Et₂O (5 cm³). The product does not have bands at 2 240 cm⁻¹ [ν(NCO)], but has i.r. bands at 2 084, 1 971, and 850 cm⁻¹ which are indicative of *trans*-[Ir(PPh₃)₂(CO)(NCS)].

Attempted Isomerization of [Rh(PPh₃)₂(CS)(NCO)] and [Rh(PPh₃)₂(CO)(NCS)].—A sample of *trans*-[Rh(PPh₃)₂(CS)(NCO)] (50 mg) was heated under reflux in toluene (20 cm³) for 15 h. The solvent was removed *in vacuo*, and the i.r. spectrum of the residue indicated no reaction. Similar treatment of *trans*-[Rh(PPh₃)₂(CO)(NCS)] indicated no reaction. A sample of *trans*-[Rh(PPh₃)₂(CS)(NCO)] (63 mg) in acetone (25 cm³) was stirred under 30 lbf in⁻² CO for 15 h. The i.r. spectrum of the product recovered after removal of the solvent *in vacuo* indicated that under the conditions of the experiment the isocyanate does not attack the co-ordinated CS.

RESULTS AND DISCUSSION

An i.r. spectral study revealed that the addition of CO to solutions of *trans*-[Rh(PPh₃)₂(CS)(N₃)] in chloroform results in rapid disappearance of the absorption band at 1 300 cm⁻¹ due to ν(CS) with concomitant appearance of a band at 1 989 cm⁻¹ due to ν(CO). A band at 2 072 cm⁻¹ due to ν_{sym}(N₃) is shifted to 2 092 cm⁻¹ due to ν(CN). Similarly, the addition of CO to *trans*-[Ir(PPh₃)₂(CS)(N₃)] results in rapid disappearance of the ν(CS) at 1 325 cm⁻¹ concomitant with a shift to higher energy of the ν_{asym}(N₃) band at 2 070 cm⁻¹ and the appearance of two bands at 1 943 and 1 989 cm⁻¹ due to ν(CO) for [Ir(PPh₃)₂(CO)₂(NCS)]. One molecule of CO is reversibly lost from the latter complex. The absence of absorption in the 2 235 and 1 353 cm⁻¹ regions in the spectra of the above reaction solutions indicated that the isocyanato-(M-NCO) complexes were not formed. The isothiocyanato-complexes *trans*-[M(PPh₃)₂(CO)(NCS)] (4; M = Rh or Ir) which were isolated and characterized by microanalysis have i.r. spectra which are consistent with the M-NCS structure shown previously.⁷ The ν(CN) for M-NCS square-planar complexes follows the order [NCS]⁻ < M-NCS < M-SCN.⁷ The reactions thus

proceed to form the isothiocyanato-complexes (4) rather than the isocyanato-complexes.



Infrared spectra (cm⁻¹) (Nujol)

C. complex	ν(CS)	ν _{asym} (N ₃)	ν _{sym} (N ₃)
[Rh(PPh ₃) ₂ (CS)(N ₃)]	1 300 ^a	2 072	1 345
[Ir(PPh ₃) ₂ (CS)(N ₃)]	1 325 ^a	2 070, 2 082 ^a	1 350
	ν(CO)	ν(CN)	ν(CS)
[Rh(PPh ₃) ₂ (CO)(NCS)]	1 989, ^a 1 984	2 092, ^a 2 075	830w
[Ir(PPh ₃) ₂ (CO)(NCS)]	1 973, ^a 1 971	2 090, ^a 2 084	850w
[Ir(PPh ₃) ₂ (CO) ₂ (NCS)]	1 978, ^a 1 943 ^a 1 971, 1 945	2 093, ^a 2 085	850w
	ν(CS) or (CO)	ν _{asym} (NCO)	ν _{sym} (NCO)
[Ir(PPh ₃) ₂ (CO)(NCO)]	1 989 ^b	2 239 ^b	1 340 ^b
[Rh(PPh ₃) ₂ (CO)(NCO)]	1 957 ^b	2 230 ^b	1 353 ^b
[Rh(PPh ₃) ₂ (CS)(NCO)]	1 300 ^b	2 240	1 340

^a In CHCl₃. ^b In KBr.

A plausible mechanistic path for the reaction would be the formation of a cationic carbonyl complex such as [M(PPh₃)₂(CS)(CO)₂][N₃] (M = Rh or Ir), followed by nucleophilic attack of the co-ordinated thiocarbonyl (CS) ligand by the azide ion.⁸⁻¹⁰ The cationic complexes [Ir(PPh₃)₂(CS)(CO)₂]⁺ and [Ir(PPh₃)₂(CO)₂]⁺ have previously been described.^{6,11} We observed that the addition of sodium azide to [Ir(PPh₃)₂(CS)(CO)₂][ClO₄] results in azide attack on the co-ordinated CS instead of CO. This preference for CS by azide ion is in contrast to the observation⁶ that sodium methoxide reacts with the carbonyl rather than the thiocarbonyl in [Ir(PPh₃)₂(CS)(CO)₂]⁺.

Carbonylation of *trans*-[M(PPh₃)₂(CO)X] (X = Cl, Br, or I) in non-polar solvents or in the absence of halogen abstracting agents, however, does not give the cationic complexes [M(PPh₃)₂(CO)₂]⁺, but instead gives the five-co-ordinate complexes [Ir(PPh₃)₂(CO)₂X] (X = Cl, Br, or I).¹² The corresponding rhodium complexes have not been observed. The present results do not exclude the possibility that the reaction proceeds by rapid ligand exchange¹³ whereby azide ion in a solvent cavity would attack the co-ordinated thiocarbonyl ligand. It was of interest to determine whether intramolecular rearrangement of atoms in ligands, such as the isomerization of *trans*-[Rh(PPh₃)₂(CS)(NCO)] to *trans*-[Rh(PPh₃)₂(CO)(NCS)], would take place. The arrangement was not observed in refluxing toluene or in acetone under CO pressure. The cyanate ion is known to react with [Fe(η-C₅H₅)(CS)(CO)₂]⁺ to give [Fe(η-C₅H₅)(CO)₂(CN)].⁸

The most likely path for the reaction would involve the formation of the five-co-ordinate intermediate [M(PPh₃)₂(CS)(CO)(N₃)] (3) analogous to the CO adducts [Ir(PPh₃)₂(CO)₂X] (X = Cl, Br, or I)¹² and [Ir(PPh₃)₂(CS)(CO)Cl].¹⁴ In the present study, the addition of CO to [Ir(PPh₃)₂(CS)(N₃)] was found to give the five-co-ordinate complex [Ir(PPh₃)₂(CO)₂(NCS)] which reversibly loses one molecule of CO. Rearrangement of [M(PPh₃)₂(CS)(CO)(N₃)] (3) can then proceed with dinitro-

gen expulsion and nitrogen-atom migration ('insertion') to the CS rather than the CO ligand. Similar preferential migration of a hydride ligand to a co-ordinated CS to form a thioformyl ligand rather than migration to a co-ordinated CO (to form a formyl ligand) has been reported in the reaction of CO with $[\text{Os}(\text{PPh}_3)_2(\text{CS})(\text{CO})\text{H}]$.¹⁵ Photoelectron spectral measurements and molecular-orbital calculations indicate that the occupied σ and π levels of CS interact more strongly with the metal and that the electron density of the carbon of the CS ligand is greater than that of the CO.¹⁶ Interestingly, where alkyl or aryl migration to the carbon atom of CO is well known, the corresponding migration to CS is still not known. The present proposed nitrogen-atom migration mechanism, instead of a path involving dissociation of and nucleophilic attack by azide ion to form a thio-cyanate ligand, is at the present stage speculative and requires further definition.

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