Carbonylation of Azido(thiocarbonyl) Complexes of Rhodium and Iridium

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The reactions of CO with *trans*-$[M(PPh_3)_2(CS)(N_3)]$ (M = Ir or Rh) in benzene or chloroform solution result in the formation of *trans*-$[M(PPh_3)_2(CO)(NCS)]$ rather than *trans*-$[M(PPh_3)_2(CS)(NCO)]$. 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 $[M(PPh_3)_2(N_3)_2]$ (M = Pt or Pd), $[M(PPh_3)_2(CO)(N_3)]$ (M = Rh or Ir), $[Rh(PPh_3)_3(N_3)]$, $[Au(PPh_3)(N_3)]$, and $[Pd(N_3)_4]^{2-}$ give isocyanatometal complexes.[1-3] Azido-complexes of

$$M{-}N_3 + CO \longrightarrow M{-}NCO + N_2 \qquad (1)$$

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 $[Pd(PR_3)_2(N_3)_2]$ 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]

$$CO + [Pd(PR_3)_2(N_3)_2] \longrightarrow \underset{(1)}{[Pd(PR_3)_2(CO)(N_3)_2]} \longrightarrow [Pd(PR_3)_2(N_3(N_3)(NCO)] \qquad (2)$$

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).

$$CO + \underset{(2)}{trans\text{-}[M(PPh_3)_2(CS)(N_3)]} \longrightarrow \underset{(3)}{[M(PPh_3)_2(CS)(CO)(N_3)]} \qquad (3)$$

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*-$[Ir(PPh_3)_2(CS)Cl]$,[4] *trans*-$[Rh(PPh_3)_2(CS)Cl]$,[5] $[Ir(PPh_3)_2(CS)(CO)_2][ClO_4]$,[6] *trans*-$[Rh(PPh_3)_2(CO)(NCO)]$,[2] and *trans*-$[Ir(PPh_3)_2(CO)(NCO)]$ [2] were synthesized using methods previously described (Found: C, 64.95; H, 4.40; N, 1.95. Calc. for $C_{38}H_{30}NO_2P_2Rh$: C, 65.45; H, 4.35; N, 2.00. Found: C, 58.05; H, 3.95; N, 1.75; P, 7.80. Calc. for $C_{38}H_{30}IrNO_2P_2$: C, 58.0; H, 3.85; N, 1.80; P, 7.85%).

Infrared-spectral Studies.—Carbon monoxide was bubbled into solutions of *trans*-$[M(PPh_3)_2(CS)(N_3)]$ (M = Rh or Ir) (10 mg) in chloroform (2 cm^3) 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*-$[M(PPh_3)_2(CO)(NCS)]$. Similar spectral studies conducted on the reactions of CO with $[Pt(PPh_3)_2(N_3)_2]$ and $[M(PPh_3)_2(CO)(N_3)]$ (M = Rh or Ir) indicated a slower rate of disappearance of the azido-complexes [$\nu(N_3)$ 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*-$[Rh(PPh_3)_2(CS)Cl]$ (192 mg), $Na[N_3]$ (400 mg), and PPh_3 (250 mg) in dichloromethane (20 cm^3) and methanol (20 cm^3) was heated under reflux for 2 h. The solvent was removed *in vacuo* and the yellow solid was washed successively with Et_2O (10 cm^3), water (10 cm^3), and MeOH (10 cm^3). The yellow product was recrystallized from CH_2Cl_2 (5 cm^3) and Et_2O (10 cm^3), yield 90%, m.p. 175 °C (decomp.) (Found: C, 62.4; H, 4.40; N, 5.75. Calc. for $C_{37}H_{30}N_3P_2RhS$: C, 62.3; H, 4.25; N, 5.90%).

trans-*Azido(thiocarbonyl)bis(triphenylphosphine)iridium*(I).—A mixture of *trans*-$[Ir(PPh_3)_2(CS)Cl]$ (464 mg), $Na[N_3]$ (504 mg), and PPh_3 (200 mg) in benzene (40 cm^3) and methanol (40 cm^3) 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 Et_2O. The yellow solid was recrystallized from chloroform–methanol, yield 364 mg (78%) (Found: C, 54.95; H, 3.95; N, 6.20. Calc. for $C_{37}H_{30}IrN_3P_2S$: C, 55.35; H, 3.75; N, 5.25%).

trans-*Carbonyl(isothiocyanato)bis(triphenylphosphine)rhodium*(I).—A solution of *trans*-$[Rh(PPh_3)_2(CS)(N_3)]$ (80 mg) in benzene (20 cm^3) 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 cm^3) and methanol (10 cm^3), yield 90%, m.p. 170—171 °C (decomp.) (Found: C, 64.15; H, 4.30; N, 2.05. Calc. for $C_{38}H_{30}NOP_2RhS$: C, 63.95; H, 4.25; N, 1.95%). This complex has been previously prepared by metathetical displacement of Cl in *trans*-$[Rh(PPh_3)_2(CO)Cl]$.[7]

trans-*Carbonyl(isothiocyanato)bis(triphenylphosphine)iridium*(I).—A solution of *trans*-$[Ir(PPh_3)_2(CS)(N_3)]$ (138 mg) in chloroform (20 cm^3) 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 $C_{38}H_{30}IrNOP_2S$: C, 56.85; H, 3.75; N, 1.75%).

Carbonylation of trans-$[Ir(PPh_3)_2(CO)(NCS)]$.—Carbon monoxide was bubbled into a solution of *trans*-$[Ir(PPh_3)_2$-

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† 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 cm^3) until the solvent was completely evaporated. The yellow product was washed with Et_2O (5 cm^3) and dried in a stream of nitrogen. The product [Ir(PPh_3)$_2$(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(PPh_3)$_2$(CO)(NCS)].

trans-*Isocyanato(thiocarbonyl)bis(triphenylphosphine)-rhodium*(I).—A mixture of *trans*-[Rh(PPh_3)$_2$(CS)Cl] (415 mg), Na[NCO] (509 mg), and PPh_3 (258 mg) in MeOH (40 cm^3) and PhH (40 cm^3) 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 cm^3), water (5 cm^3), EtOH (5 cm^3), and Et_2O (10 cm^3). The product was recrystallized as yellow crystals (90%) from $CHCl_3$–EtOH (Found: C, 63.8; H, 4.25; N, 1.85. Calc. for $C_{38}H_{30}NOP_2RhS$: C, 63.95; H, 4.25; N, 1.95).

Reaction of [Ir(PPh_3)$_2$(CS)(CO)$_2$][ClO_4] *with Sodium Azide.*—A solution of Na[N_3] (10.4 mg) in water (2 cm^3) was added to [Ir(PPh_3)$_2$(CS)(CO)$_2$][ClO_4] (55.9 mg) in acetone (5 cm^3). There was immediate N_2 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 cm^3), and Et_2O (5 cm^3). 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(PPh_3)$_2$(CO)(NCS)].

Attempted Isomerization of [Rh(PPh_3)$_2$(CS)(NCO)] *and* [Rh(PPh_3)$_2$(CO)(NCS)].—A sample of *trans*-[Rh(PPh_3)$_2$(CS)(NCO)] (50 mg) was heated under reflux in toluene (20 cm^3) 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(PPh_3)$_2$(CO)(NCS)] indicated no reaction. A sample of *trans*-[Rh(PPh_3)$_2$(CS)(NCO)] (63 mg) in acetone (25 cm^3) 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(PPh_3)$_2$(CS)(N_3)] 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 $\nu_{sym}(N_3)$ is shifted to 2 092 cm^{-1} due to ν(CN). Similarly, the addition of CO to *trans*-[Ir(PPh_3)$_2$(CS)(N_3)] results in rapid disappearance of the ν(CS) at 1 325 cm^{-1} concomitant with a shift to higher energy of the $\nu_{asym}(N_3)$ 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(PPh_3)$_2$(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(PPh_3)$_2$(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.

$$\textit{trans}\text{-}[M(PPh_3)_2(CS)(N_3)] + CO \longrightarrow \underset{(4)}{\textit{trans}\text{-}[M(PPh_3)_2(CO)(NCS)]} + N_2 \quad (4)$$

Infrared spectra (cm^{-1}) (Nujol)

Complex	ν(CS)	$\nu_{asym}(N_3)$	$\nu_{sym}(N_3)$
[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 $CHCl_3$. [b] In KBr.

A plausible mechanistic path for the reaction would be the formation of a cationic carbonyl complex such as [M(PPh_3)$_2$(CS)(CO)$_2$][N_3] (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(PPh_3)$_2$(CS)(CO)$_2$]$^+$ and [Ir(PPh_3)$_2$(CO)$_3$]$^+$ have previously been described.[6,11] We observed that the addition of sodium azide to [Ir(PPh_3)$_2$(CS)(CO)$_2$][ClO_4] results in azide attack on the co-ordinated CS instead of CO. This preference for CS by azide ion is in contrast to the observation [6] that sodium methoxide reacts with the carbonyl rather than the thiocarbonyl in [Ir(PPh_3)$_2$(CS)(CO)$_2$]$^+$.

Carbonylation of *trans*-[M(PPh_3)$_2$(CO)X] (X = Cl, Br, or I) in non-polar solvents or in the absence of halogen-ion abstracting agents, however, does not give the cationic complexes [M(PPh_3)$_2$(CO)$_2$]$^+$, but instead gives the five-co-ordinate complexes [Ir(PPh_3)$_2$(CO)$_2$X] (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 exchange [13] 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(PPh_3)$_2$(CS)(NCO)] to *trans*-[Rh(PPh_3)$_2$(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-C_5H_5)(CS)(CO)$_2$]$^+$ to give [Fe(η-C_5H_5)(CO)$_2$(CN)].[8]

The most likely path for the reaction would involve the formation of the five-co-ordinate intermediate [M(PPh_3)$_2$(CS)(CO)(N_3)] (3) analogous to the CO adducts [Ir(PPh_3)$_2$(CO)$_2$X] (X = Cl, Br, or I) [12] and [Ir(PPh_3)$_2$(CS)(CO)Cl].[14] In the present study, the addition of CO to [Ir(PPh_3)$_2$(CS)(N_3)] was found to give the five-co-ordinate complex [Ir(PPh_3)$_2$(CO)$_2$(NCS)] which reversibly loses one molecule of CO. Rearrangement of [M(PPh_3)$_2$(CS)(CO)(N_3)] (3) can then proceed with dinitrogen 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 [Os$(PPh_3)_2$(CS)(CO)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 thiocyanate ligand, is at the present stage speculative and requires further definition.

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