

Ovine III-Thrift in Nova Scotia. Part 10.† Palladium and Rhodium Complexes as Reagents in the Investigation of Isocyanide Metabolites of *Trichoderma hamatum*

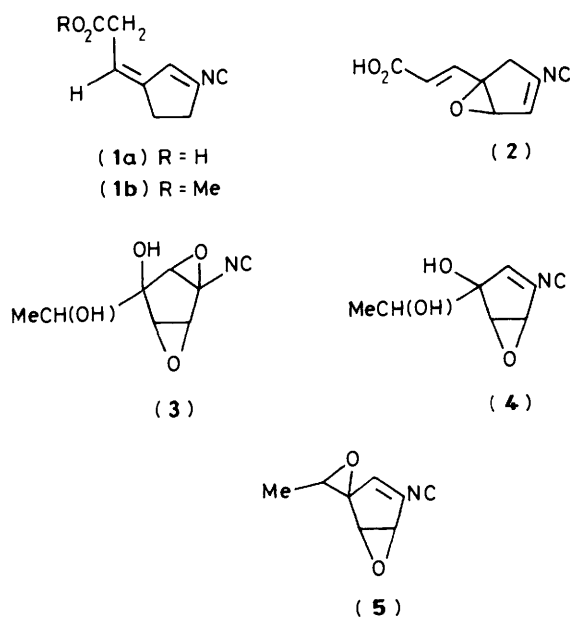
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Spectroscopic studies indicate that the reaction of the methyl ester (**1b**) of the fungal metabolite 3-(3-isocyanocyclopent-2-enylidene)propionic acid (**1a**) with dichlorobis- μ -[methylenebis(diphenylphosphine)]-dipalladium(i) (**6**), to give the product of insertion of the isocyano function into the Pd-Pd bond, is accompanied by C=C bond isomerisation. That the crystalline material thus obtained did contain the bridging isocyanide moiety as in the expected insertion product [**7**; RNC = (**1b**)] was confirmed by X-ray crystallographic analysis. Reaction of (**1b**) with di- μ -chloro-dichlorobis(η^5 -pentamethylcyclopentadienyl)dirhodium(III) (**8**) or bis(η^5 -pentamethylcyclopentadienyl)bis-(μ -thiocyanato-*N,S*)-bis(thiocyanato-*S*)dirhodium(III) (**9**) gave the monomeric 1:1 adducts (**10**) and (**11**). The results of X-ray crystallographic analysis of (**11**), which displays greater thermal stability than the chloro analogue (**10**), support the assignment of structure (**1b**) to the isocyanide ligand, in agreement with earlier conclusions based on spectroscopic evidence.

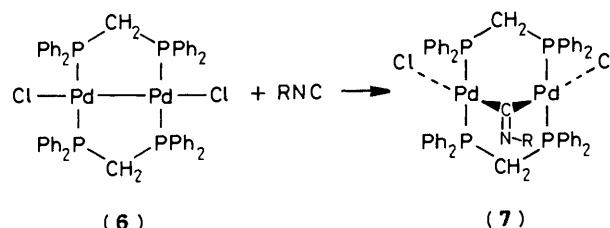
Fungi of the genus *Trichoderma* have been found¹⁻⁴ to provide a number of unstable cyclopentanoid metabolites [*e.g.* (**1a**), (**2**)—(**5**)] all of which are thought to possess an isocyanide group. Most of these metabolites have antibiotic activity^{4,5} but the unusual and unstable isocyano acids [*e.g.* (**1a**)] inhibit the growth and metabolism of certain rumen bacteria at concentrations of *ca.* 1×10^8 g ml⁻¹.⁵ They are, therefore, as possible parameters in the phenomenon of ill-thrift,⁶ of potential agricultural importance. Accordingly, we have become interested in developing methods for their isolation, characterisation, and quantification.^{3,5,7} The metabolite (**1a**) is the most inhibitory isocyanide isolated so far, but it is also very unstable. The structure (**1a**) depends heavily on interpretation

talline derivatives. It seemed possible that this might be done by using them as ligands in a suitable transition-metal complex. Our choice of metal derivatives was dictated by the requirements that complex formation should be rapid under mild conditions; that it should be feasible in the presence of aqueous media, to facilitate isolation from culture filtrates; and finally that the stability constants of the complexes formed should ensure survival during purification procedures but should allow displacement of the isocyanide ligand without degradation or rearrangement. Not all of these requirements have been met, but stable crystalline derivatives of (**1b**) have been prepared and X-ray diffraction data have been collected that support the structure of (**1b**) and hence of the parent acid (**1a**).



Results and Discussion

(i) *Reaction of (1b) with [Pd₂(μ -Ph₂PCH₂PPh₂)₂Cl₂] (6).*—The diphosphine-bridged dimetallic palladium(i) complex (**6**) has been reported⁹ to react with simple isocyanides *via* insertion into the Pd-Pd bond to give (**7**) as illustrated in the Scheme. We have found that dropwise addition of a solution of



Scheme.

(**1b**) in diethyl ether to a solution of (**6**) in dichloromethane results in the immediate deposition of a finely crystalline yellow product which can be recrystallised from dichloromethane. This product tended to darken gradually on storage, the rate of darkening increasing noticeably on prolonged exposure to light. We have been unable to find a report in the literature of similar behaviour for simple isocyanide complexes of the type (**7**). The recrystallised material gave elemental analyses and an electronic spectrum (see Experimental section) consistent with those expected for the insertion product [**7**; RNC = (**1b**)]. The i.r. spectrum showed the expected carbonyl absorption (1734,

of spectroscopic data and on a slightly ambiguous synthesis.^{8a} Thus satisfactory characterisation of this compound and its less stable congeners requires their conversion into stable, crys-

† Part 9 is ref. 5.

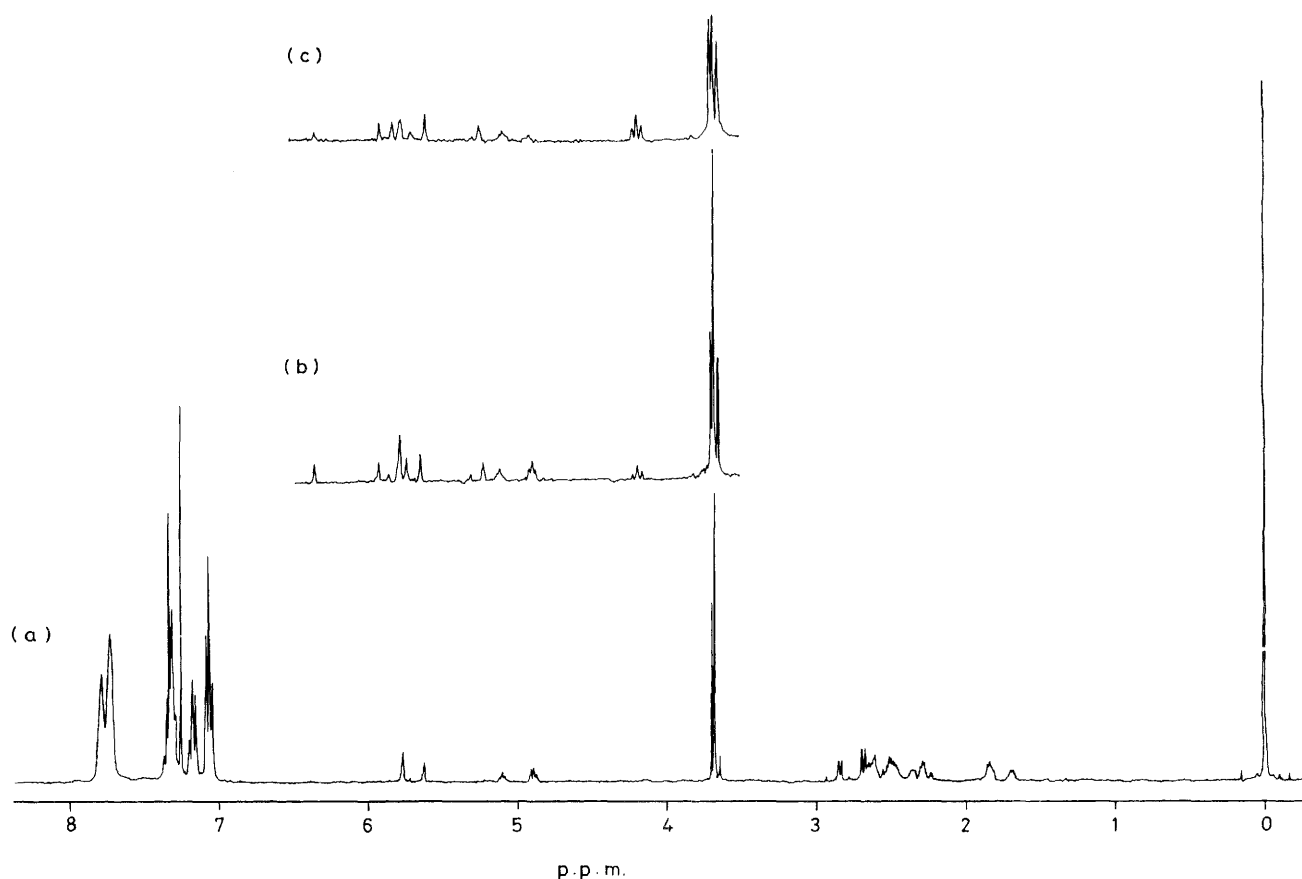


Figure 1. ^1H N.m.r. spectra of [7; $\text{RN}=\text{C} = (\mathbf{1b})$]; (a) spectrum of the recrystallised product, (b) partial spectrum of crystalline material used for X-ray diffraction studies, (c) partial spectrum of specimen (b) after heating

1722sh, cm^{-1}), and a band (1657 cm^{-1}) near the region where peaks attributed to $\nu(\text{C}=\text{N})$ in complexes of type (7) have been reported previously.⁹ However, this band probably arises from adsorbed water¹⁰ (*cf.* spectrum of a second sample of the product discussed below), and absorption at lower energies ($1568, 1562\text{ cm}^{-1}$) may be due to $\nu(\text{C}=\text{N})$.¹⁰ The ^1H n.m.r. spectrum (Figure 1a) showed resonances attributable to two major species, and at least two minor ones, clearly demonstrating that a pure sample of the expected product [7; $\text{RNC} = (\mathbf{1b})$] had not been obtained. Since the electronic spectrum was consistent with the formation of a product of this type, a reasonable explanation for the complex nature of the ^1H n.m.r. spectrum could be that olefinic bond isomerisation had taken place within the isocyanide moiety. Such isomerisation could have been promoted by small amounts of Pd^{II} -containing species in the reaction mixture, since it is known¹¹ that this type of reaction is catalysed by palladium(II) derivatives.

Since it was also possible that isomerisation had been facilitated by heating during recrystallisation of the complex obtained above, the preparation was repeated with the proportion of the solvents adjusted to allow the slow separation of larger orange-yellow crystals. The product thus obtained had the same electronic spectrum as the previous preparation, while the i.r. spectrum showed no band at *ca.* 1650 cm^{-1} . However, its ^1H n.m.r. spectrum (Figure 1b), which showed peaks attributable to the same two major isomers as before, was more complex. When this sample was heated, the peaks corresponding to the more abundant major isomer underwent a considerable, and irreversible decrease in relative intensity, but there was no significant development of new resonances (Figure 1c). The behaviour on

heating allows us to discount the possibility that the major species are related by slow rotation (on the n.m.r. time scale), about the five-membered ring C–N bond in [7; $\text{RNC} = (\mathbf{1b})$]. A proton-noise-decoupled ^{31}P n.m.r. spectrum showed a single peak, which along with the electronic spectrum indicates that there is only one type of palladium co-ordination environment in the sample, supporting the suggestion that the complicated ^1H n.m.r. spectra result from olefin isomerisation.

Further support for the conclusion that isocyanide-bridged species of the kind [7; $\text{RNC} = (\mathbf{1b})$] had been obtained was provided by X-ray crystallography. A view of the resulting molecular structure is given in Figure 2 and selected bond lengths and angles are collected in Table 1. Although the precision of the analysis was relatively low (see Experimental section), and the methoxycarbonyl group could not be located, it is considered adequate to establish that the carbon skeleton of the ligand ($\mathbf{1b}$) is correctly depicted, that N(1) is in fact nitrogen rather than carbon, that C(4) is bonded to both Pd atoms, and that the C(4)–N(1)–C(3') angle is 132° . The precision of the data does not permit distinction between double and single bonds in the isocyanide ligand, but the location of C(3) indicates *Z* geometry if the C(1')–C(3) bond is olefinic, in accord with previous spectroscopic measurements.^{8b} The analysis does not preclude the possibility that the corresponding *E* isomer could also be present; its presence would be consistent with the low value found in the electron density map for the C(2) peak, and with the ^1H n.m.r. data.

A remarkable feature of the crystal structure is the continuous channel, *ca.* 10 \AA in diameter, extending along the 4₁ axis at $\frac{1}{2}, \frac{1}{2}, z$ (Figure 3). Surprisingly, such channels have

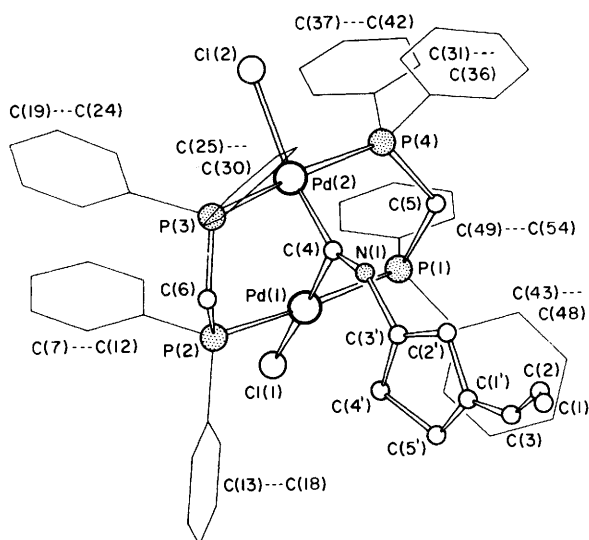


Figure 2. A view of [7; RN=C = (1b)]

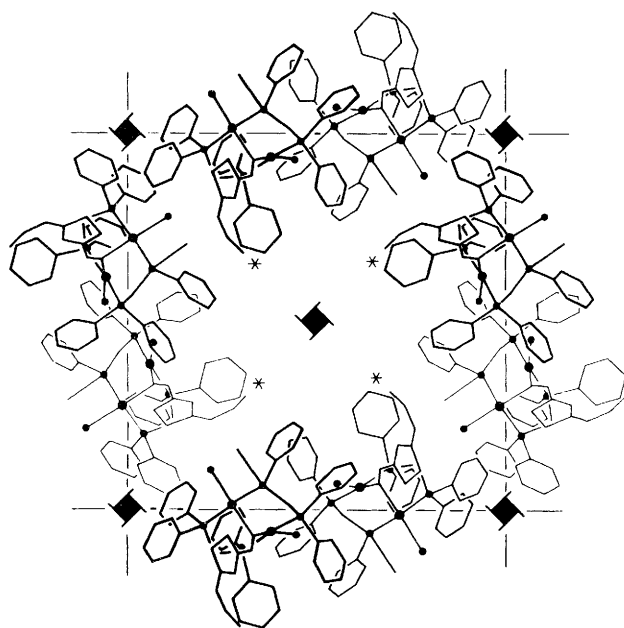


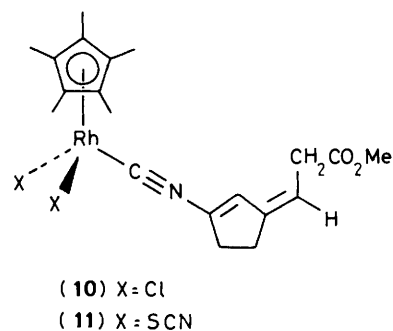
Figure 3. Projection of [7; RN=C = (1b)] along the *c*-axis (the asterisks indicate the presumed positions of the methoxycarbonyl groups, which could not be located)

not excited comment in previous reports of crystallographic analyses of isostructural compounds.¹² It can be seen from Figure 3 that the methoxycarbonyl group of the isocyanide ligand extends into the channel, and thus is allowed almost unrestrained thermal motion, consequently making location of this group difficult.

(ii) *Reaction of (1b) with* [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\}_2$] (**8**) *and with* [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{SCN})_2\}_2$] (**9**).—The dimeric rhodium(III) complex (**8**) and the corresponding bromo and iodo derivatives have been reported^{13,14} to react readily with simple isocyanides (RNC) to give the air-stable monomeric adducts [$\eta^5\text{-C}_5\text{Me}_5\text{Rh}(\text{RNC})\text{X}_2$] ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Isocyanide adducts have also been obtained from the azido analogue [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{N}_3)_2\}_2$].¹⁵ The reaction of (**1b**) with (**8**) could be followed by t.l.c. on silica impregnated with sodium chloride; omission of

the salt led to tailing solutes. Presumably the salt suppresses dissociation of chloride from the rhodium derivatives.¹⁶ The adduct (**10**) could be purified by p.l.c. and was obtained as dull red crystals from diethyl ether–dichloromethane. The constitution of (**10**) was supported by elemental analysis and spectroscopic properties. In particular, the ¹H n.m.r. spectrum contained signals attributable to the ligand (**1b**) that were similar to those observed for the unco-ordinated compound, which suggested that no isomerisation of (**1b**) had taken place in the course of complexation.

Complex (**10**) appears to be relatively stable in the solid state. However solutions in dichloromethane tend to darken when allowed to stand at ambient temperature, presumably owing to liberation and subsequent polymerisation of (**1b**), since the dimeric complex (**8**) could be recovered on chromatography of such solutions. Relatively rapid decomposition was observed when a dichloromethane solution of (**10**) was evaporated under reduced pressure at a bath temperature of 30–35 °C. It was, therefore, desirable to find a less labile analogue of the adduct (**10**). The report¹⁷ that the reaction of [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhI}_2\}_2$] with carbon monoxide gives an identifiable though labile, complex [$(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})\text{I}_2$] while no such complex was observed with the chloro analogue (**8**), combined with the view that isocyanides can bond in a similar manner,¹⁸ suggested that more stable adducts of (**1b**) might be obtained from dimers of the type [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{X})_2\}_2$] where Rh–X has greater covalent character than Rh–Cl. The complex [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{SCN})_2\}_2$]¹⁵ (**9**) was found to run without tailing on silica gel plates, unlike its chloro (**8**) or iodo analogues. When solutions of (**1b**) and the thiocyanato complex (**9**) were mixed



and the reaction mixture was examined by t.l.c., a new compound less polar than (**9**) was observed. This product could be purified by p.l.c., and crystallisation from acetone–diethyl ether gave rosettes of long orange needles (**11**) which proved suitable for X-ray crystallographic analysis.

A view of the resulting molecular structure is shown in Figure 4, and selected bond lengths and angles are given in Table 2. The data confirm that the adduct has the expected structure (**11**) in which the exocyclic C=C bond of the isocyanide ligand has the *Z* configuration. It may be noted that the C(4)–N(1)–C(3') angle is 178° as is usual for terminally bound isocyanides,¹⁸ and that the thiocyanato groups are bound to rhodium *via* the S atoms, as has been proposed¹³ for the analogous adduct [$(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CNC}_6\text{H}_{11})(\text{SCN})_2$] on the basis of its i.r. spectrum.

Spectroscopic and analytical data for (**11**) are given in the Experimental section. Notably the ¹H n.m.r. data for (**11**) and for (**10**) are similar, lending support to the assignment of structure (**10**). As anticipated, the thiocyanato derivative (**11**) is more robust than its chloro analogue (**10**). Thus solutions of (**11**) in dichloromethane can be heated to boiling, or left overnight at ambient temperature without significant decom-

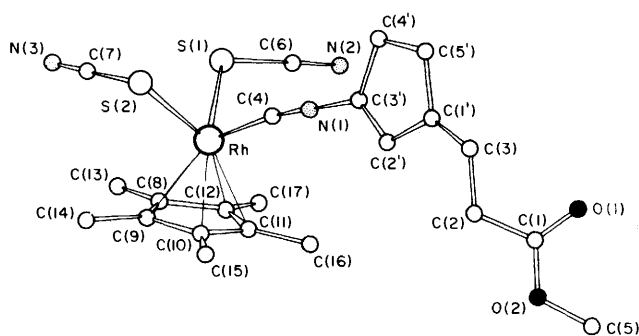


Figure 4. A view of (11)

osition, although analytical t.l.c. of such solutions indicates the presence of traces of the dimer (9).

In conclusion, complex (9) appears to be a promising candidate as a reagent for forming relatively stable derivatives of isocyanide metabolites produced by *Trichoderma* species. Work is in progress on the application of (9) to the isolation and characterisation of further metabolites, and on the regeneration of the metabolites from their complexes.

Experimental

Electronic and i.r. spectra were run on Cary 14 and Perkin-Elmer 283B spectrophotometers respectively. Proton, and ^1H broad band decoupled ^{31}P n.m.r. spectra were recorded on the Nicolet 360 NB spectrometer of the Atlantic Region Magnetic Resonance Centre, Halifax, Nova Scotia. Chemical shifts are expressed in p.p.m. relative to internal tetramethylsilane for the former and to external 85% H_3PO_4 for the latter, with positive shifts indicating deshielding. For analytical t.l.c., commercial plates (Kieselgel 60 F_{254} , Merck) were used as received, or after being dipped in 10% w/v aqueous sodium chloride followed by air drying and then activation for 2 h at 110 °C. For preparative t.l.c. (p.l.c.) plates (20 × 20 × 0.05 cm) were spread with Kieselgel 60 GF_{254} (Merck), or a 20:1 (w/w) mixture of this silica and sodium chloride. Melting points are uncorrected. Solutions (ca. 3.5 mg cm^{-3}) of (1b)⁵ in diethyl ether were stored at -15 °C. Complexation reactions using this solution, and subsequent examination by t.l.c. were performed without special precautions to exclude air. Solvents were reagent grade, and used as received.

Reaction of $[\text{Pd}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Cl}_2]$ (6) with the Ester (1b).—(a) A cold (0 °C) solution of (1b) (ca. 7 mg) in diethyl ether (2 cm^3) was added dropwise with stirring during 1 min to a solution of the complex (6)¹⁹ (60 mg) in dichloromethane (6 cm^3) at ambient temperature to give a finely crystalline yellow precipitate which was collected, and washed with dichloromethane–diethyl ether (1:1; 3 × 2 cm^3), and then dissolved and washed through the filter by repeated digestion with warm dichloromethane. The resulting solution was evaporated to ca. 8 cm^3 (water bath, 50–60 °C) and then allowed to stand at ambient temperature to give very fine, light orange-yellow needles. After being washed with dichloromethane–diethyl ether (1:1; 3 × 2 cm^3) and dried *in vacuo*, these [7; R = CN-($\text{C}_9\text{H}_{11}\text{O}_2$)] (38 mg) had m.p. 196–199 °C (decomp.). (Found: C, 58.45; H, 4.7; Cl, 5.85; N, 1.25; P, 9.85%. $\text{C}_{60}\text{H}_{55}\text{Cl}_2\text{NO}_2\text{P}_4\text{Pd}_2$ requires C, 58.6; H, 4.50; Cl, 5.75; N, 1.15; P, 10.05%); $\lambda_{\text{max.}}(\text{CH}_2\text{Cl}_2)$ 294, 395sh, and 446 nm (ϵ 34 100, 7 440, and 13 300 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\nu_{\text{max.}}(\text{Nujol})$ 1 734, 1 722sh, 1 657, 1 568, and 1 562 cm^{-1} ; ^1H n.m.r., see Figure 1a.

(b) A solution of the methyl ester (1b) (ca. 12 mg) in diethyl

ether (3.5 cm^3) was evaporated at 0 °C to ca. 0.5 cm^3 , and cold (0 °C) dichloromethane (1.5 cm^3) was added. The resulting solution was added dropwise to the complex (6)¹⁹ (70 mg) dissolved in dichloromethane (6 cm^3) to give an orange solution from which, when it was set aside at ambient temperature, orange-yellow crystals were deposited. The mixture was kept overnight at -15 °C after which the supernatant liquid was removed and the residue washed with diethyl ether–dichloromethane (3:2; 2 × 1 cm^3) and then with ether (2 × 1 cm^3) to give orange-yellow crystals (53 mg), m.p. 195–197 °C (decomp.); $\lambda_{\text{max.}}(\text{CH}_2\text{Cl}_2)$ 294, 395sh, and 446 nm (ϵ 34 400, 7 400, and 13 200 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\nu_{\text{max.}}(\text{Nujol})$ 1 734, 1 723sh, 1 597, 1 590, 1 569, and 1 562 cm^{-1} ; ^1H n.m.r. at ambient temperature and after ca. 1 h at 60 °C, see Figures 1b and 1c; ^{31}P { ^1H } n.m.r. (C^2HCl_3) δ 15.60 s—on heating to 60 °C this peak moved to 16.11 and three new resonances of low relative intensities (each 2–5% of the main peak) developed at 16.35, 16.43, and 16.84 over ca. 1 h at this temperature.

Reaction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ (8) with (1b).—A cold (0 °C) solution of the ester (1b) (ca. 35 mg) in diethyl ether (10 cm^3) was added to a solution of the complex (8)¹⁷ (75 mg) in dichloromethane (20 cm^3). P.l.c. (NaCl-impregnated SiO_2 ; eluant, methanol–dichloromethane, 3:37) of the resulting mixture gave two orange-red bands which were eluted with methanol–dichloromethane (1:1), the more polar band giving the starting complex (8). The eluate from the less polar band was evaporated under reduced pressure, the bath temperature being kept below 15 °C, to give an orange-red residue which was crystallised from dichloromethane–diethyl ether (-15 °C) to give the adduct (10) (54 mg) as dull red crystals, m.p. 150–153 °C (Found: C, 48.05; H, 5.4; Cl, 16.2; N, 2.9; O, 6.45; Rh, 20.9%. $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{NO}_2\text{Rh}$.0.15 CH_2Cl_2 requires C, 48.5; H, 5.30; Cl, 16.35; N, 2.80; O, 6.40; Rh, 20.6%); $\nu_{\text{max.}}(\text{CH}_2\text{Cl}_2)$ 2 162s ($\text{N}=\text{C}$); 1 740s cm^{-1} ($\text{C}=\text{O}$); ^1H n.m.r. (C^2HCl_3) δ 1.81 (s, 15 H, CMe), 2.68–2.80 (symmetrical m, 4 H, CH_2CH_2), 3.14 (d, 2 H, J 7.7 Hz, $\text{CH}_2\text{CH}=\text{}$), 3.70 (s, 3 H, OMe), 5.31 (s, (CH_2Cl_2), 5.52 (t, J 7.7 Hz, $=\text{CHCH}_2$), and 6.68 (br s, H, olefinic H).

Reaction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{SCN})_2]_2$ (9) with (1b).—A cold (0 °C) solution of (1b) (ca. 18 mg) in diethyl ether (5 cm^3) was added to a solution of the complex (9)¹⁵ (50 mg) in dichloromethane (10 cm^3) at ambient temperature. P.l.c. of the resulting solution (eluant methanol–dichloromethane, 1:39) gave two yellow-orange bands which were eluted with acetone, the more polar band giving the starting complex (9) (13 mg). The residue from the less polar band (52 mg), on crystallisation from acetone–diethyl ether, gave the adduct (11) (35 mg) as rosettes of long orange-yellow needles, m.p. 130–132 °C (Found: C, 49.75; H, 4.90; N, 7.90; O, 6.10; Rh, 19.1; S, 11.9%. $\text{C}_{22}\text{H}_{26}\text{N}_3\text{O}_2\text{RhS}$ requires C, 49.7; H, 4.95; N, 7.90; O, 6.00; Rh, 19.35; S, 12.05%); $\nu_{\text{max.}}(\text{CH}_2\text{Cl}_2)$ 2 160s ($\text{N}=\text{C}$), 2 106s (SCN), 1 738s and 1 723sh ($\text{C}=\text{O}$) cm^{-1} ; ^1H n.m.r. (C^2HCl_3) δ 1.90 (s, 15 H, CMe), 2.69–2.89 (symmetrical m, 4 H, CH_2CH_2), 3.13 (d, 2 H, J 7.5 Hz $\text{CH}_2\text{CH}=\text{}$), 3.70 (s, 3 H, OMe), 5.53 (t, 1 H, J 7.5 Hz, $=\text{CHCH}_2$), and 6.79 (s, H, olefinic).

X-Ray Crystallography.—**Crystal data.** (i) Palladium complex (single-crystal photographs and diffractometry, with $\text{Cu-K}\alpha$, $\lambda = 1.5418 \text{ \AA}$, at $T = 24 \text{ }^\circ\text{C}$), orange needles (c) $\text{C}_{60}\text{H}_{55}\text{Cl}_2\text{NO}_2\text{P}_4\text{Pd}_2$, $M = 1 229.7$, tetragonal, $a = 21.44(1)$, $c = 14.236(6) \text{ \AA}$, $U = 6 544 \text{ \AA}^3$, $D_m = 1.44 \text{ g cm}^{-3}$ (variable from crystal to crystal, and with time as the channels fill with the flotation medium; the value given is for material immersed for several days in a flotation medium of CCl_4 –light petroleum, and is regarded as an upper limit), $Z = 4$, $D_c = 1.248 \text{ g cm}^{-3}$, $F(000) = 2 496$, $\mu = 6.5 \text{ mm}^{-1}$, space group $P4_1$ (or $P4_3$) (C_4^2 or C_4^4 , No. 76 or 78).

(ii) Rhodium complex (11), orange needles (*c*), $C_{22}H_{26}N_3O_2RhS_2$, $M = 531.5$, monoclinic, $a = 22.706(3)$, $b = 15.091(3)$, $c = 7.072(1)$ Å, $\beta = 92.48(2)^\circ$, $U = 2421.0$ Å³, $D_m = 1.455$ g cm⁻³ (floatation in CCl₄-light petroleum), $Z = 4$, $D_c = 1.458$ g cm⁻³, $F(000) = 1088$, $\mu = 7.6$ mm⁻¹, space group $P2_1/a$ (C_2^{5h} , No. 14, systematic absences hOl for h odd, OkO for k odd).

Intensity Measurement, Structure Determination, and Refinement.—A specimen of the palladium complex, of dimensions $0.08 \times 0.11 \times 0.22$ mm, was mounted with the long (needle) axis approximately parallel to the ϕ -axis of the (Picker 4-circle) diffractometer. The unit cell constants were determined by least-squares analysis of the diffractometer settings of 13 well-centred reflections with $51 < 2\theta < 81^\circ$. The relative intensities of the independent reflections with $2\theta < 100^\circ$ were measured with Ni-filtered radiation. The θ - 2θ scan method was used, and individual reflection profiles were analysed as described by Grant and Gabe.²⁰ The intensity of a standard reflection (110) was measured at intervals of 60 reflections, and was found to decrease by *ca.* 30% during the measurement period. (A comparable loss of scattering power occurs even without irradiation.) The measured intensities were appropriately adjusted, assuming the decrease in scattering power to be linear between standard measurements, and equivalent for all reflections. The standard deviations were evaluated from the counts; reflections with $I_{net} > 3\sigma(I_{net})$ were classed as 'observed' and were used in the analysis. These numbered 2209 of a possible 3553. Absorption corrections (Gaussian integration), ranging from 1.54 to 1.89, were applied to the intensities.

The Pd, Cl, and P atoms were readily located by heavy-atom methods. A Fourier synthesis, phased on their contributions,

Table 1. Selected interatomic distances and angles for [7; RNC = (1b)] (Å and °; e.s.d.'s in parentheses)

Pd(1)···Pd(2)	3.198(4)	C(2)–C(3)	1.60(9)
Pd(1)–Cl(1)	2.454(9)	C(3)–C(1')	1.37(7)
Pd(2)–Cl(2)	2.460(11)	C(1')–C(2')	1.41(7)
Pd(1)–P(1)	2.370(9)	C(2')–C(3')	1.44(5)
Pd(1)–P(2)	2.337(10)	C(3')–C(4')	1.58(6)
Pd(2)–P(3)	2.311(10)	C(4')–C(5')	1.60(7)
Pd(2)–P(4)	2.349(11)	C(5')–C(1')	1.55(6)
Pd(1)–C(4)	2.12(3)	C(3')–N(1)	1.42(5)
Pd(2)–C(4)	1.81(4)	N(1)–C(4)	1.21(5)
P(1)–C(5)	1.96(3)	Pd(1)–C(4)–Pd(2)	109(2)
P(2)–C(6)	1.92(3)	N(1)–C(4)–Pd(1)	123(3)
P(3)–C(6)	1.78(4)	N(1)–C(4)–Pd(2)	127(3)
P(4)–C(5)	1.81(4)	C(3')–N(1)–C(4)	133(3)
C(1)–C(2)	1.69(10)		

Table 2. Selected interatomic distances and angles for (11) (Å and °; e.s.d.'s in parentheses)

Rh–S(1)	2.399(4)	O(2)–C(5)	1.45(2)
Rh–S(2)	2.392(4)	C(1)–C(2)	1.52(2)
Rh–C(4)	1.96(1)	C(2)–C(3)	1.48(2)
Rh–C(8)	2.21(1)	C(3)–C(1')	1.35(2)
Rh–C(9)	2.20(1)	C(1')–C(2')	1.44(2)
Rh–C(10)	2.17(1)	C(2')–C(3')	1.32(2)
Rh–C(11)	2.19(1)	C(3')–C(4')	1.49(2)
Rh–C(12)	2.18(1)	C(4')–C(5')	1.56(2)
S(1)–C(6)	1.64(2)	C(5')–C(1')	1.52(2)
S(2)–C(7)	1.68(2)	C(3')–N(1)	1.41(2)
N(2)–C(6)	1.17(2)	N(1)–C(4)	1.14(2)
N(3)–C(7)	1.14(2)	C(3')–N(1)–C(4)	176(1)
C(1)–O(1)	1.20(2)	Rh–C(4)–N(1)	171(1)
C(1)–O(2)	1.31(2)		

Table 3. Atomic co-ordinates (e.s.d.'s) for [7; RNC = (1b)]. (Phenyl ring carbon atoms are in idealised positions, which were not refined)

	<i>x</i>	<i>y</i>	<i>z</i>
Pd(1)	0.721 17(11)	0.015 87(11)	0.000 0*
Pd(2)	0.615 67(11)	–0.059 02(12)	0.112 0(3)
Cl(1)	0.783 5(4)	0.111 9(4)	–0.000 2(9)
Cl(2)	0.547 5(4)	–0.067 7(5)	0.250 5(9)
P(1)	0.796 9(4)	–0.043 0(4)	0.082 8(7)
P(2)	0.638 2(4)	0.064 4(4)	–0.077 5(8)
P(3)	0.538 5(4)	–0.019 3(4)	0.015 6(8)
P(4)	0.694 1(4)	–0.113 2(5)	0.193 5(8)
N(1)	0.668 2(12)	–0.107 4(12)	–0.045 8(20)
C(1')	0.746 1(19)	–0.173 7(19)	–0.242 3(36)
C(2')	0.709 9(18)	–0.182 7(18)	–0.160 4(32)
C(3')	0.708 4(16)	–0.120 7(16)	–0.122 4(30)
C(4')	0.736 1(19)	–0.067 3(18)	–0.186 7(32)
C(5')	0.770 8(23)	–0.107 7(23)	–0.265 6(40)
C(1)	0.688 5(28)	–0.296 1(29)	–0.424 3(49)
C(2)	0.710 3(30)	–0.279 6(32)	–0.312 9(50)
C(3)	0.756 4(25)	–0.221 5(25)	–0.304 3(40)
C(4)	0.668 5(15)	–0.067 1(14)	0.013 6(27)
C(5)	0.767 4(15)	–0.122 9(15)	0.132 6(27)
C(6)	0.565 2(15)	0.013 5(15)	–0.091 8(25)
C(7)	0.6083	0.1306	–0.0188
C(8)	0.6318	0.1488	0.0680
C(9)	0.6062	0.1998	0.1144
C(10)	0.5571	0.2326	0.0740
C(11)	0.5336	0.2143	–0.0128
C(12)	0.5592	0.1633	–0.0593
C(13)	0.6583	0.0917	–0.1910
C(14)	0.6949	0.1444	–0.2049
C(15)	0.7093	0.1638	–0.2956
C(16)	0.6871	0.1304	–0.3725
C(17)	0.6505	0.0776	–0.3586
C(18)	0.6361	0.0583	–0.2679
C(19)	0.4844	0.0406	0.0583
C(20)	0.4950	0.0653	0.1473
C(21)	0.4531	0.1079	0.1853
C(22)	0.4008	0.1259	0.1344
C(23)	0.3902	0.1012	0.0454
C(24)	0.4321	0.0585	0.0074
C(25)	0.4917	–0.0842	–0.0185
C(26)	0.4519	–0.0791	–0.0953
C(27)	0.4214	–0.1317	–0.1294
C(28)	0.4307	–0.1893	–0.0869
C(29)	0.4705	–0.1944	–0.0100
C(30)	0.5010	–0.1419	0.0241
C(31)	0.6750	–0.1917	0.2168
C(32)	0.7189	–0.2391	0.2090
C(33)	0.7001	–0.3011	0.2120
C(34)	0.6373	–0.3157	0.2227
C(35)	0.5933	–0.2683	0.2305
C(36)	0.6122	–0.2062	0.2275
C(37)	0.7119	–0.0868	0.3057
C(38)	0.7549	–0.1121	0.3681
C(39)	0.7738	–0.0783	0.4464
C(40)	0.7497	–0.0190	0.4623
C(41)	0.7067	0.0064	0.4000
C(42)	0.6878	–0.0275	0.3217
C(43)	0.8579	–0.0664	0.0032
C(44)	0.8800	–0.0266	–0.0665
C(45)	0.9282	–0.0458	–0.1251
C(46)	0.9544	–0.1047	–0.1140
C(47)	0.9323	–0.1444	–0.0443
C(48)	0.8840	–0.1253	0.0142
C(49)	0.8374	–0.0089	0.1842
C(50)	0.8849	–0.0407	0.2304
C(51)	0.9116	–0.0154	0.3109
C(52)	0.8910	0.0417	0.3451
C(53)	0.8435	0.0735	0.2989
C(54)	0.8167	0.0482	0.2184

* Held constant during refinement.

Table 4. Atomic co-ordinates (e.s.d.'s) for non-hydrogen atoms (11)

	x	y	z
Rh	0.190 24(4)	0.086 90(7)	0.042 65(14)
S(1)	0.155 8(2)	0.180 9(3)	0.288 6(6)
S(2)	0.273 9(2)	0.051 4(3)	0.244 6(6)
O(1)	-0.080 9(4)	-0.424 3(7)	-0.111 2(15)
O(2)	-0.042 0(5)	-0.412 4(7)	-0.392 7(14)
N(1)	0.122 0(4)	-0.077 6(7)	0.172 8(14)
N(2)	0.033 5(6)	0.153 5(12)	0.267 5(21)
N(3)	0.329 0(7)	0.217 2(12)	0.289 4(22)
C(1)	-0.040 5(6)	-0.406 2(9)	-0.208 1(24)
C(2)	0.019 1(6)	-0.376 5(10)	-0.125 4(23)
C(3)	0.022 1(6)	-0.359 1(9)	0.081 4(22)
C(4)	0.149 0(5)	-0.016 7(9)	0.139 4(16)
C(5)	-0.095 7(7)	-0.445 8(11)	-0.486 7(24)
C(6)	0.084 3(7)	0.166 4(12)	0.275 9(22)
C(7)	0.303 2(7)	0.152 7(12)	0.270 2(21)
C(8)	0.212 1(5)	0.189 6(9)	-0.167 0(17)
C(9)	0.246 2(5)	0.109 5(9)	-0.200 8(18)
C(10)	0.206 3(6)	0.039 8(10)	-0.240 8(17)
C(11)	0.147 0(5)	0.070 4(9)	-0.237 1(17)
C(12)	0.149 7(5)	0.164 0(9)	-0.189 3(17)
C(13)	0.236 0(7)	0.282 2(9)	-0.127 7(22)
C(14)	0.311 6(5)	0.105 9(12)	-0.204 5(21)
C(15)	0.223 3(8)	-0.055 9(10)	-0.291 0(22)
C(16)	0.090 8(6)	0.021 0(13)	-0.284 5(21)
C(17)	0.098 1(7)	0.227 8(12)	-0.183 7(23)
C(1')	0.046 7(5)	-0.288 4(8)	0.169 5(20)
C(2')	0.074 0(5)	-0.214 2(9)	0.079 1(18)
C(3')	0.091 5(5)	-0.156 8(9)	0.211 1(18)
C(4')	0.078 2(6)	-0.179 4(9)	0.409 8(19)
C(5')	0.051 1(5)	-0.273 6(9)	0.382 6(19)

revealed much of the rest of the structure, but with poor resolution of the phenyl groups. These were, therefore, treated as regular hexagons, of side 1.395 Å, so located as to match the electron density. The 48 phenyl C atoms, together with the two well-resolved bridging methylene C atoms, were included in a further structure-factor calculation. The subsequent Fourier synthesis revealed 10 atoms (all but the terminal methoxy-carbonyl group) of the isocyanide moiety (and in addition provided revised locations for the phenyl groups, still treated as regular hexagons). Reiteration of this procedure, incorporating the 10 additional atoms, revealed no more significant peaks. It seems likely that the intense thermal motion of the terminal methoxycarbonyl group renders it inconspicuous against the background noise of the electron-density map [$\sigma(\rho) = 1.6 \text{ e } \text{Å}^{-3}$]. The highest peak in the 10-atom fragment [N(1)] was at $6.8 \text{ e } \text{Å}^{-3}$, and the lowest [C(2)] at $2.4 \text{ e } \text{Å}^{-3}$. The (incomplete) structure was refined by block-diagonal least squares, minimising $\sum w \Delta F^2$ where $1/w = \sigma^2(F_o) + 0.001 F_o^2$. The parameters varied were: scale factor; temperature factors for all atoms (anisotropic for Pd, Cl, and P); co-ordinates of all atoms except phenyl C. The final R index was 0.084 (observed reflections only; $R_w = 0.112$).

A specimen of the rhodium complex (11) of dimensions $0.025 \times 0.06 \times 0.4 \text{ mm}$ was mounted as for the palladium complex, above; 34 reflections ($44 < 2\theta < 54^\circ$) were used to determine the unit-cell constants. The independent reflections with $2\theta < 130^\circ$ were measured with graphite-monochromatised radiation. The θ - 2θ scan method was used, but without profile analysis; the scan range was $(1.4 + 0.284 \tan \theta)^\circ$, and background intensities were measured for one tenth of the scan duration at each end of the range. The intensity of a standard reflection (120, measured at intervals of 60 reflections) was found to decrease by ca. 18% during the procedure, and the

measured intensities were scaled as for the palladium complex, above. The reflections used in the analysis [$I_{\text{net}} > 3\sigma(I_{\text{net}})$] numbered 1 815 of a possible 4 136. Absorption corrections (1.21 to 1.70) were applied to the measured intensities.

The structure was readily solved by heavy-atom methods. Refinement was by block-diagonal least squares, as for the palladium complex above. Hydrogen atoms (other than methyl) were included in the structure-factor calculations with parameters reasonably assumed, but not refined. The parameters varied were: scale factor, atomic co-ordinates, and temperature factors (anisotropic for Rh, Cl, and P). The final R index was 0.058 (observed reflections only; $R_w = 0.070$).

The atomic co-ordinates of the non-H atoms of the palladium and rhodium complexes are given in Tables 3 and 4, and selected bond lengths and angles in Tables 1 and 2. Views of the molecular structures are given in Figures 1 and 3. The computer program system has been described by Larson and Gabe.²¹ The atomic scattering factors were taken from ref. 22. Co-ordinates of hydrogen atoms, temperature factors of all atoms, and bond lengths not given in the paper are available as a Supplementary publication [SUP No. 56123 (10 pp.)].* The Structure Factor listings are available on request from the Editorial office.

* For details of the Supplementary publications scheme, see Instructions to Authors (1985), *J. Chem. Soc., Perkin Trans. I*, 1985, Issue 1.

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