

SYNTHESIS AND REACTIONS OF RHODIUM COMPOUNDS CONTAINING TELLURIUM DONOR LIGANDS

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Summary

This paper describes the synthesis and characterization of a series of rhodium(I) and rhodium(III) complexes containing tellurium—rhodium bonds resulting from the coordination of diorgano telluride or organotelluro ligands. Oxidative addition, metathesis and substitution reactions of these compounds have been examined, and the resulting products are compared with those from the known reactions of rhodium(I) and rhodium(III) compounds containing phosphine ligands.

Introduction

Studies of rhodium and iridium complexes show that their ability to undergo oxidative addition reactions depends markedly upon the nature of the central metal atom, as well as upon the nature of the ligands. Complexes containing rhodium—phosphorus linkages are well represented in the literature, and their chemical behavior has been extensively explored. Less well known, however, are compounds of rhodium containing other ligands such as diaryl or dialkyl tellurides, and their potential utility is undetermined.

Experimental

All procedures were carried out in an argon atmosphere, using Schlenk-tube techniques. Hexane and benzene were used after distillation under nitrogen from calcium hydride, and all other solvents were used as obtained. Rhodium(III) chloride trihydrate, chlorobis(ethylene)rhodium(I) dimer and diphenyl telluride were purchased from Strem Chemicals, Inc. Carbon monoxide gas was obtained from Matheson. Diphenyl ditelluride [1] and chlorodicarbonylrhodium(I) dimer [2] were prepared by published procedures. Melting points were recorded in air and are uncorrected. Infrared spectra were measured as Nujol mulls and were recorded on a Perkin-Elmer 567 grating IR spectrophotometer.

Chlorocarbonylbis(diphenyl telluride)rhodium(I)

A 25% excess of diphenyl telluride (14.1 g, 50 mmol) was added to a suspension of chlorodicarbonylrhodium(I) dimer (3.98 g, 10 mmol) in 150 ml of hexane. The solution immediately darkened and was stirred at room temperature for 24 h. The resulting precipitate was filtered, washed with hexane and vacuum dried to yield 13.7 g (94%) of a chocolate-brown solid, m.p. 158–159°C.

Carbonyl(diphenyl telluride)thiocyanatorhodium(I) dimer

A solution of potassium thiocyanate (0.097 g, 1 mmol) in 20 ml of methanol was added to a solution of chlorocarbonylbis(diphenyl telluride)rhodium(I) (0.73 g, 1 mmol) in 150 ml of methylene chloride. The solution was stirred at room temperature for 3 h and filtered. The filtrate was evaporated to dryness and the residue was recrystallized from methylene chloride/ether to yield 0.35 g (95%) of a brown solid, m.p. grad. dec. above 50°C.

Chlorotris(diphenyl telluride)rhodium(I)

Chlorobis(ethylene)rhodium(I) dimer (5.0 g, 12.9 mmol) was added to a solution of diphenyl telluride (65.2 g, 230 mmol) in 300 ml of hot methanol. The solution was heated at reflux for 30 min and 300 ml of ether was added. After an additional 4 h reflux period, no precipitate was present. The solvent was evaporated under vacuum, and the oily red residue was crystallized by the addition of hexane with stirring. The resulting solid was filtered, washed with hexane and vacuum dried to yield 13.7 g (54%) of a red solid, m.p. grad. dec. above 85°C.

Chlorobis(diphenyl telluride)rhodium(I) dimer

1. Heptaldehyde (0.5 ml) was added to a solution of chlorotris(diphenyl telluride)rhodium(I) (0.5 g, 0.5 mmol) in 10 ml of benzene. The solution was heated at reflux for 1 h and then stirred at room temperature for 24 h. The product was precipitated with 20 ml of hexane, filtered, washed with hexane and dried to yield 0.25 g (71%) of a red solid, m.p. dec. above 125°C.

2. A solution of chlorotris(diphenyl telluride)rhodium(I) (0.5 g, 0.5 mmol) in 15 ml of carbon disulfide was heated at reflux for 15 min, cooled to room temperature and then stirred at room temperature for 2 h. The carbon disulfide was removed under vacuum and the residue was recrystallized from benzene/hexane to yield 0.3 g (86%) of the same red solid.

3. An excess of hexafluoro-2-butyne was condensed (–78°C) onto a frozen solution of chlorotris(diphenyl telluride)rhodium(I) (0.5 g, 0.5 mmol) in 10 ml of benzene in a pressure tube. The tube was capped, warmed to room temperature and allowed to stand for 24 h. The tube was then cooled to –78°C and opened. The contents of the tube was reduced to dryness under vacuum, and the residue was recrystallized from benzene/hexane to yield 0.3 g (86%) of a red solid.

Trichlorotris(diphenyl telluride)rhodium(III)

Diphenyl telluride (16.91 g, 60 mmol) was added to a solution of rhodium(III) chloride trihydrate (2.63 g, 10 mmol) in 200 ml of ethanol. The solu-

tion was heated for 22 h, cooled to room temperature and mixed with 200 ml of hexane. The resulting precipitate was filtered, washed well with ether and dried to yield 7.9 g (75%) of an orange-red solid, m.p. 197–199°C.

Carbonylbis(diphenyl telluride)trichlororhodium(III)

Carbon monoxide gas was bubbled through a solution of trichlorotris-(diphenyl telluride)rhodium(III) (0.46 g, 0.436 mmol) in 75 ml of chloroform for 24 h. The solution was filtered, evaporated to half volume and mixed with 100 ml of hexane. The resulting precipitate was filtered, washed with hexane and dried to yield 0.25 g (69%) of a red solid, m.p. 163–165°C.

Carbonylchlorodibromobis(diphenyl telluride)rhodium(III)

A solution of bromine (0.16 g, 1 mmol) in 10 ml of benzene was added to a solution of chlorocarbonylbis(diphenyl telluride)rhodium(I) (0.73 g, 1 mmol) in 75 ml of benzene. The solution was stirred at room temperature for 3 h, filtered and concentrated to half of the original volume. Addition of 75 ml of hexane precipitated a solid, which was filtered, washed with hexane and dried to yield 0.4 g (45%) of a red solid, m.p. 136–138°C.

Carbonylchlorodiodobis(diphenyl telluride)rhodium(III)

A solution of iodine (0.25 g, 1 mmol) in 50 ml of benzene was added to a solution of chlorocarbonylbis(diphenyl telluride)rhodium(I) (0.73 g, 1 mmol) in 75 ml of benzene. The solution was stirred at room temperature for 3 h, filtered and evaporated to about 60 ml. Addition of 60 ml of hexane gave a precipitate, which was filtered, washed with hexane and dried to yield 0.8 g (81%) of a red solid, m.p. dec. above 115°C.

Carbonylchlorobis(diphenyl telluride)bis(thiocyanato)rhodium(III)

A solution of bromine (0.24 g, 1.5 mmol) in 9 ml of carbon tetrachloride was added dropwise to a suspension of silver thiocyanate (0.498 g, 3 mmol) in 30 ml of carbon tetrachloride. When the reaction was complete, the solution was filtered and used immediately (yield, 1.5 mmol of $(\text{SCN})_2$) as follows. The fresh solution of thiocyanogen was added to a suspension of chlorocarbonylbis-(diphenyl telluride)rhodium(I) (1.09 g, 1.5 mmol) in 75 ml of carbon tetrachloride. The mixture was stirred at room temperature for 3 h and filtered. The resulting solid was recrystallized from chloroform/hexane to yield 0.7 g (55%) of a red-brown solid.

Dichloro(phenyltelluro)bis(diphenyl telluride)rhodium(III)

A solution of rhodium(III) chloride trihydrate (2.0 g, 7.6 mmol) in 120 ml hot ethanol was added to a refluxing solution of diphenyl telluride (7.75 g, 27.5 mmol) in 250 ml of ethanol. Heating was continued for 5 min and 20 ml of a 37% solution of formaldehyde in water was then added. The solution was heated at reflux for 24 h and then cooled to 0°C. The resulting precipitate was filtered, washed with hexane and dried to yield 5.25 g (73%) of a deep-red solid.

Carbonyldichloro(phenyltelluro)bis(diphenyl telluride)rhodium(III)

Carbon monoxide gas was bubbled through a solution of dichloro(phenyl-

telluro)bis(diphenyl telluride)rhodium(III) (0.94 g, 1 mmol) in 50 ml of benzene for 3 h. The solvent was removed under vacuum and the resulting solid was recrystallized from methylene chloride/hexane to yield 0.5 g (52%) of a red solid.

Tris(diphenyltelluro)rhodium(III)

A solution of rhodium(III) chloride trihydrate (0.415 g, 1.58 mmol) in 40 ml of hot ethanol was added to a boiling solution of diphenyl telluride (4.5 g, 15.9 mmol) in 160 ml of ethanol. A 40% solution of formaldehyde in water (16 ml) and a solution of potassium hydroxide (1.28 g) in 40 ml of hot ethanol were added successively. The reaction mixture was heated at reflux for 30 min and cooled to room temperature. Filtration yielded 0.95 g (84%) of a dark-brown solid.

Results and discussion

A variety of synthetic routes have now been explored for the preparation of complexes containing rhodium—tellurium bonds. For certain types of complexes rhodium—tellurium products obtained by a particular procedure are strictly analogous to those products which could be isolated in rhodium—phosphine chemistry. In other cases, however, different chemical behavior is observed on substitution of organotellurium for organophosphine ligands. In this initial study, three types of rhodium complexes were sought in order to evaluate the effect of replacement of triphenylphosphine by diphenyl telluride as the ligand (i.e., $L_2Rh(CO)Cl$, L_3RhCl and $L_3Rh(CO)H$, where $L = Ph_2Te$). Analytical data for each of the rhodium—tellurium complexes prepared are given in Table 1.

An initial attempt to prepare $(Ph_2Te)_3RhCl$ via the reaction of rhodium(III) chloride trihydrate with excess diphenyl telluride gave instead $(Ph_2Te)_3RhCl_3$ as a deep-red solid (eq. 1).



The related phosphine complex $(Ph_3P)_3RhCl_3$ can also be prepared by a reaction between rhodium(III) chloride trihydrate and a stoichiometric amount of triphenylphosphine [3], but the use of an excess of triphenylphosphine results in reduction of the metal and isolation of the rhodium(I) complex $(Ph_3P)_3RhCl$ [4].

Several reactions of the complex $(Ph_2Te)_3RhCl_3$ were examined. Bubbling carbon monoxide gas through a solution of the compound in chloroform for 24 h led to the isolation of $(Ph_2Te)_2(CO)RhCl_3$ (eq. 2), a complex in which one



telluride ligand was replaced by CO. No di- or trisubstituted products were observed. Reaction of $(Ph_2Te)_3RhCl_3$ with methyl lithium or sodium borohydride led to complex reaction mixtures, the components of which remain unidentified.

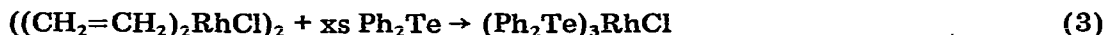
Chlorotris(diphenyl telluride)rhodium(I) was prepared via the substitution

TABLE 1
ANALYTICAL DATA FOR COMPLEXES

| Compound | Analysis Found (calcd.) (%) | | | | | | | Mol. wt. ^a Found (calcd.) |
|---|-----------------------------|---------------|---------------|-----------------|---------------|-----------------|-----------------|--|
| | C | H | N | Cl | S | Rh | Te | |
| (Ph ₂ Te) ₂ Rh(CO)Cl | 40.9 (41.13) | 3.2 (2.76) | | 4.6 (4.86) | | 14.4 (14.10) | 36.4 (35.96) | 710 (730) |
| (Ph ₂ TeRh(CO)(CNS)) ₂ | 35.9 (35.72) | 2.3 (2.14) | 2.8 (2.97) | | 6.2 (6.81) | 21.5 (21.86) | 27.9 (27.10) | 705 (736) |
| (Ph ₂ Te) ₃ RhCl | 43.4 (43.95) | 3.3 (3.07) | | 3.5 (3.60) | | 10.7 (10.46) | 38.9 (38.91) | 614 (984) |
| ((Ph ₂ Te) ₂ RhCl) ₂ | 41.1 (41.06) | 2.9 (2.87) | | 5.1 (5.05) | | 14.9 (14.66) | 36.9 (36.35) | 685 (702) |
| (Ph ₂ Te) ₃ RhCl ₃ | 40.8 (41.00) | 2.7 (2.87) | | 10.4 (10.08) | | 10.1 (9.76) | 36.5 (36.29) | 920 (1055) |
| (Ph ₂ Te) ₂ (CO)RhCl ₃ | 37.4 (37.49) | 2.5 (2.52) | | | | 12.7 (12.85) | 31.4 (31.86) | 780 (801) |
| (Ph ₂ Te) ₂ Rh(CO(C)Cl)Br ₂ | 33.9 (33.75) | 2.3 (2.27) | | 4.3 (3.98) | | 11.4 (11.56) | 28.6 (28.68) | 850 (890) |
| (Ph ₂ Te) ₂ Rh(CO)ClI ₂ | 30.4 (30.52) | 2.1 (2.05) | | 3.1 (3.60) | | 10.8 (10.46) | 25.9 (25.94) | 940 (984) |
| (Ph ₂ Te) ₂ Rh(CO)Cl(CNS) ₂ | 38.1 (38.33) | 2.5 (2.38) | 3.8 (3.31) | 3.9 (4.19) | 7.9 (7.58) | 12.4 (12.16) | 30.4 (30.16) | 800 (846) |
| (Ph ₂ Te) ₂ Rh(TePh)Cl ₂ | 38.6 (38.25) | 2.5 (2.67) | | 7.5 (7.53) | | 10.7 (10.92) | 40.2 (40.63) | 905 (942) |
| (Ph ₂ Te) ₂ Rh(CO)(TePh)Cl ₂ | 38.3 (38.38) | 2.5 (2.60) | | 7.8 (7.31) | | 10.9 (10.61) | 38.9 (39.46) | |
| Rh(TePh) ₃ | 30.1 (30.15) | 2.1 (2.11) | | | | 14.7 (14.35) | 52.9 (53.39) | |

^a 1,2-dichloroethane solution at 25°C.

reaction between diphenyl telluride and the labile chlorobis(ethylene)rhodium(I) dimer (eq. 3). The chemistry of the red solid was compared with the known chemistry of the phosphine analogue (Ph₃P)₃RhCl (Table 2).



Triphenylphosphine is known to react with [Rh(CO)₂Cl]₂ to give (Ph₃P)₂Rh(CO)Cl [9]. The reaction of diphenyl telluride with the chlorodicarbonylrhodium(I) dimer also gives a carbonyl complex of this type (eq. 4). One similar compound (where L = Et₂Te) is known [10]. This complex and several of its

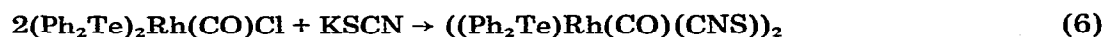
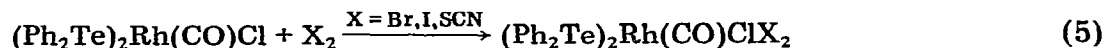
TABLE 2
COMPARISON OF THE REACTIVITY OF (Ph₃P)₃RhCl AND (Ph₂Te)₃RhCl

| Reagent | Product from (Ph ₂ Te) ₃ RhCl and reagent | Product from (Ph ₃ P) ₃ RhCl and reagent |
|--------------------------------------|---|--|
| CO | Complex mixture of carbonylated products with broad ν _{CO} bands at 1950–2040 cm ⁻¹ . | (Ph ₃ P) ₂ Rh(CO)Cl [4,5] |
| n-C ₆ H ₁₃ CHO | No CO abstraction, ((Ph ₂ Te) ₂ RhCl) ₂ obtained | (Ph ₃ P) ₂ Rh(CO)Cl [5] |
| CS ₂ | No CS abstraction, ((Ph ₂ Te) ₂ RhCl) ₂ obtained | (Ph ₃ P) ₂ Rh(CS)Cl [6] |
| CF ₃ C≡CCF ₃ | No alkyne substitution, ((Ph ₂ Te) ₂ RhCl) ₂ obtained | (Ph ₃ P) ₂ Rh(CF ₃ C≡CCF ₃) [7] |
| CH ₃ I | No reaction | (Ph ₂ P) ₂ RhCH ₃ I ₂ [8] |

reaction products are the only examples of rhodium complexes with tellurium donor ligands reported prior to this work.



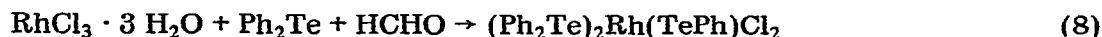
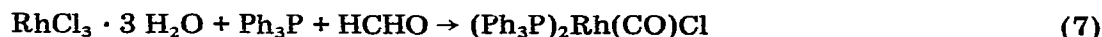
Several oxidative addition and metathetical reactions have been carried out with chlorocarbonylbis(diphenyl telluride)rhodium(I).



Bromine, iodine and thiocyanogen all react with the rhodium(I) complex to give good yields of the corresponding rhodium(III) derivative. These results correlate well with those obtained using chlorocarbonylbis(triphenylphosphine)rhodium(I) as the starting material, except that bromine does not react with the latter compound. Chlorocarbonylbis(diphenyl telluride)rhodium(I) and methyl iodide do not react; however, chlorocarbonylbis(diethyl telluride)rhodium(I) oxidatively adds methyl iodide to yield $(\text{Et}_2\text{Te})_2\text{Rh}(\text{CO})\text{ClMeI}$, a compound which, unlike the phosphine derivative, is inert to CO insertion into the rhodium—methyl bond. Furthermore, HCl gas does not react with $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{Cl}$ to yield the expected $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{Cl}_3$. However, this compound has been prepared by another route (eq. 2).

Finally, $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$ can be rapidly converted to the bromide, iodide or thiocyanate by the reaction in acetone solution at room temperature with lithium bromide, sodium iodide or potassium thiocyanate, respectively [11]. A similar simple metathesis reaction was not observed between $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{Cl}$ and potassium thiocyanate, a dimeric compound being obtained instead (eq. 6).

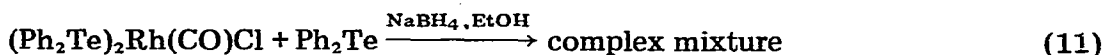
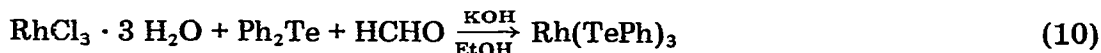
An alternative preparation of chlorocarbonylbis(diphenyl telluride)rhodium(I) was attempted using rhodium—phosphine chemistry as a model (eq. 7). This reaction (eq. 8) did not give a product analogous to that in eq. 7. A good



yield of the rhodium(III) complex containing two chloro and one phenyltelluro ligands was isolated instead in an unusual reaction in which a tellurium—carbon bond of the ligand is severed. This compound reacts with carbon monoxide gas in solution to give the product in eq. 9.



Two different reactions were evaluated in the attempt to prepare the diphenyl telluride analog of $(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})\text{H}$ [12,13], and these are outlined in eqs. 10 and 11. $(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})\text{H}$ has been prepared using modifications of



both of these routes; however, the reactions proceed quite differently with diphenyl telluride as a ligand and no well-defined products were isolated from the reaction shown in eq. 11. $(\text{PhTe})_3\text{Rh}$ has been isolated in 84% yield as an insoluble polymeric material following the procedure outlined in eq. 10. This compound illustrates a second example of tellurium-carbon bond cleavage of the ligand in reactions with rhodium compounds. Cleavage of one or both carbon-tellurium bonds in reactions of diphenyl telluride with either manganese or cobalt compounds has been reported to yield $[\text{Mn}(\text{CO})_4\text{TePh}]_2$ and $[\text{Co}_2(\text{CO})_5\text{Te}]_n$, respectively [14]. Interaction of $(\text{PhTe})_3\text{Rh}$ with carbon monoxide in solution yielded a complex mixture of products with broad $\nu(\text{CO})$ absorptions at 1970–2040 cm^{-1} .

Rhodium complexes containing organotellurium ligands isolated in this work are generally red to red-brown solids, which are soluble in a variety of organic solvents and appear to be air stable in the solid state. In general, the color of a particular tellurium-ligand-containing complex is much darker than that of its triphenylphosphine analog (e.g., $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{Cl}$ is a chocolate-brown solid, whereas $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$ is a yellow solid). Many of the complexes do not have sharp melting points either in air (melting-point tube) or under nitrogen (DSC data), but rather decompose gradually over an extended temperature range. The temperatures at which gross decomposition under nitrogen (by TGA) begins for each complex are listed in Table 3.

Infrared spectra (Nujol mull) have been recorded for each compound; $\nu(\text{CO})$ and $\nu(\text{CN})$ absorptions are recorded in Table 4. Published data for several similar compounds containing diethyl telluride as a ligand are included for comparison [10]. One interesting point here is the relatively high value of $\nu(\text{CO})$ observed for $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{Cl}$ (2040 cm^{-1}) as compared to that seen in $(\text{Et}_2\text{Te})_2\text{Rh}(\text{CO})\text{Cl}$ (1955 cm^{-1}), indicating an increased π acidity of Ph_2Te versus Et_2Te . The position of $\nu(\text{CN})$ is of interest in that sulfur-bonded thiocyanates generally exhibit very sharp CN stretching bands in the 2130–2100 cm^{-1} region, whereas nitrogen-bonded thiocyanates exhibit much more intense, broad CN stretching bands in the range 2100–2075 cm^{-1} [15]. On the basis of the sharpness and position of $\nu(\text{CN})$ for the thiocyanate complexes prepared, we tentatively assign to them the sulfur-bonded mode. Rhodium(III)-thiocyan-

TABLE 3
THERMAL ANALYTICAL DATA FOR RHODIUM-TELLURIUM COMPOUNDS

| Compound | $T(\text{gross dec.})$ ($^{\circ}\text{C}$) |
|---|---|
| $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{Cl}$ | 117 |
| $(\text{Ph}_2\text{TeRh}(\text{CO})(\text{CNS}))_2$ | 130 |
| $(\text{Ph}_2\text{Te})_3\text{RhCl}$ | 146 |
| $((\text{Ph}_2\text{Te})_2\text{RhCl})_2$ | 138 |
| $(\text{Ph}_2\text{Te})_3\text{RhCl}_3$ | 179 |
| $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{ClBr}_2$ | 135 |
| $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{CO})\text{ClI}_2$ | 141 |
| $(\text{Ph}_2\text{Te})_2\text{RhCOCl}(\text{SCN})_2$ | 127 |
| $(\text{Ph}_2\text{Te})_2\text{Rh}(\text{TePh})\text{Cl}_2$ | 149 |
| $\text{Rh}(\text{TePh})_3$ | 155 |

TABLE 4
 INFRARED DATA FOR RHODIUM—TELLURIUM COMPOUNDS ^a

| Compound | $\nu(\text{CO})$ (cm^{-1}) | $\nu(\text{SCN})$ (cm^{-1}) |
|---|--|---|
| (Ph ₂ Te) ₂ Rh(CO)Cl | 2940 | |
| (Ph ₂ TeRh(CO)(CNS)) ₂ | 2060 | 2135 |
| (Ph ₂ Te) ₂ (CO)RhCl ₃ | 2080 | |
| (Ph ₂ Te) ₂ Rh(CO)ClBr ₂ | 2060 | |
| (Ph ₂ Te) ₂ Rh(CO)ClI ₂ | 2070 | |
| (Ph ₂ Te) ₂ Rh(CO)Cl(SCN) ₂ | 2080 | 2140 |
| (Ph ₂ Te) ₂ Rh(CO)(TePh)Cl ₂ | 2050 | |
| (Et ₂ Te) ₂ Rh(CO)Cl | 1955 [10] | |
| (Et ₂ Te) ₂ Rh(CO)Cl ₃ | 2060 [10] | |
| (Et ₂ Te) ₂ Rh(CO)ClBr ₂ | 2056 [10] | |
| (Et ₂ Te) ₂ Rh(CO)ClI ₂ | 2043 [10] | |
| (Et ₂ Te) ₂ Rh(CO)ClMeI | 2030 [10] | |

^a Taken in Nujol mull.

ate complexes generally contain SCN ligands in the S-bonded mode with $\nu(\text{CN})$ above 2100 cm^{-1} [15].

The molecular weight of chlorotris(diphenyl telluride)rhodium(I) determined in 1,2-dichloroethane solution was 614 (calcd. 984), thus indicating some dissociation of the complex in solution. When determined in similar solvents at 25°C or below, the molecular weight of chlorotris(triphenylphosphine)rhodium(I) is about half that expected, owing to dissociation of the compound to triphenylphosphine and the formally three-coordinate species (Ph₃P)₂RhCl, which has three solvent-occupied sites.

Acknowledgement

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