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COMPLEXES OF TETRACYANOETHYLENE WITH PALLADIUM AND RHODIUM ISOCYANIDE DERIVATIVES

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SUMMARY

$Pd(PhNC)_2$ reacts with an equimolar amount of tetracyanoethylene (TCNE) to give the novel isocyanide complex $Pd(PhNC)_2(TCNE)$ (I). This complex reacts readily with an excess of triphenylphosphine or triphenylarsine (EPh_3) to give the "mixed" derivative $Pd(PhNC)(EPh_3)(TCNE)$ (II); when (I) is treated with triisopropylphosphite or 1,2-bis(diphenylphosphino)ethane(Diphos), both isocyanide ligands are replaced, to yield $Pd[P(O\text{-}i\text{-}Pr)_3]_2(TCNE)$ (III) and Pd(Diphos)(TCNE) (IV), respectively.

$[Rh(PhNC)_2(PPh_3)_2]Cl$ undergoes replacement of one of the coordinated phosphines by reaction with TCNE to give the neutral complex $Rh(PhNC)_2(PPh_3)(TCNE)Cl$ (V). TCNE also replaces one isocyanide ligand in $[Rh(PhNC)_4]Cl$ to give the neutral $Rh(PhNC)_3(TCNE)Cl$ (VI). $Rh(CO)(p\text{-}MeOC_6H_4NC)_2Cl$ reacts with TCNE with replacement of coordinated carbon monoxide to give the coordinatively unsaturated complex $Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)Cl$ (VII), which can take up one mole of pyridine to give $Rh(p\text{-}MeOC_6H_4NC)_2(Pyridine)(TCNE)Cl$ (VIII). The IR spectra and reactivity of the new complexes are discussed.

INTRODUCTION

Several complexes of transitional metals with tetracyanoethylene (TCNE) have been described previously[1,2]. Use of this very strong π-acceptor has proved of great help in understanding the factors that affect the interaction of d^{10} and d^8 metal ion complexes with electrophilic addenda and the reactivity of the resultant adducts towards the replacement of other ligands present.

We have now extended the scope of these reactions by the use of isocyanides (RNC) as ligands. Most of the complexes of TCNE previously studied contain carbon monoxide as a ligand, but IR studies of the stretching frequencies of CO and RNC in mixed carbonylisocyanide derivatives indicate that isocyanides are stronger σ-donors and weaker π-acceptors than carbon monoxide[3,4]. We therefore thought it worthwhile to investigate the preparation and reactivity of some isocyanide complexes of rhodium and palladium with TCNE. Our aims were (*i*) to study the relative ability of TCNE and isocyanides as π-acceptors; (*ii*) to discuss changes of the isocyanide ν(NC) vibration upon coördination as an index of the electron density on the central metal, and (*iii*) to study the reactivity of these complexes towards monodentate and bidentate π-accepting ligands.

RESULTS AND DISCUSSION

Palladium derivatives

The phenylisocyanide complex $Pd(PhNC)_2$[5] reacts readily with TCNE in chloroform to give the adduct $Pd(PhNC)_2(TCNE)$ (I). Analytical and IR data for this as well as for the other new complexes described herein are presented in Tables 1 and 2. (I) is one of a very small number of complexes of palladium with cyanoolefins so far reported; other examples are $Pd(PPh_3)_2(TCNE)$, prepared by addition of TCNE to $Pd(PPh_3)_4$[6], and $Pd(t\text{-}BuNC)_2(TCNE)$[7], which was described in a paper which appeared while this work was in progress. The IR spectrum of (I) in the N≡C and C≡N stretching region shows two strong bands at 2232 and 2223 cm^{-1} assigned to ν(CN) of the TCNE moiety, and two very strong bands at 2198 and 2180 cm^{-1} attributable to the isocyanide ν(NC) vibrations. The large increase of this frequency in the adduct (I) relative to that in the parent compound $Pd(PhNC)_2$ (2099 cm^{-1})[8] indicates a marked reduction of electron π-back-donation from the metal to the isocyanide caused by coordination of the strongly accepting cyanoolefin. The frequency falls in the range observed for isocyanide complexes of palladium(II)[9], suggesting that the extent of electron drift to the cyanoolefin causes the formal oxidation state of the metal almost to approach the divalent state.

TABLE 1

ANALYTICAL DATA

Complex	Colour	Analysis found (calcd.) (%)			
		C	H	N	Cl
$Pd(PhNC)_2(TCNE)$	Pale-yellow	54.7	2.4	19.4	
		(54.49)	(2.29)	(19.52)	
$Pd(PhNC)(PPh_3)(TCNE)$	Pale-yellow	62.3	3.5	11.6	
		(62.06)	(3.36)	(11.68)	
$Pd(PhNC)(AsPh_3)(TCNE)$	Yellow	57.4	3.1	11.0	
		(57.82)	(3.13)	(10.88)	
$Pd[P(O\text{-}i\text{-}Pr)_3]_2(TCNE)$	Off-white	44.4	6.5	8.6	
		(44.28)	(6.49)	(8.60)	
Pd(Diphos)(TCNE)	Pale-yellow	60.7	3.8	8.9	
		(60.70)	(3.80)	(8.85)	
$Rh(PhNC)_2(PPh_3)(TCNE)Cl$	Yellow-green	62.3	3.4	11.3	5.0
		(62.09)	(3.43)	(11.44)	(4.82)
$Rh(PhNC)_3(TCNE)Cl$	Olive-green	55.8	2.7	16.8	6.2
		(56.31)	(2.63)	(17.03)	(6.16)
$Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)Cl$	Yellow-orange	49.1	2.6	15.7	6.7
		(49.59)	(2.65)	(15.78)	(6.65)
$Rh(p\text{-}MeOC_6H_4NC)_2(Py)(TCNE)Cl$	Yellow	52.6	3.2	15.9	5.9
		(52.99)	(3.13)	(16.03)	(5.79)

TABLE 2

SELECTED INFRARED BANDS OF COMPLEXES (cm^{-1})

All spectra taken as hexachlorobutadiene or Nujol mulls, unless otherwise stated; vs, very strong, s, strong; m, medium; (sh), shoulder; w, weak; br, broad.

Complex	$\nu(C\equiv N)$[a]			$\nu(N\equiv C)$[b]		Other bands	
Pd(PhNC)$_2$[c]				2099 s			
Pd(PhNC)$_2$(TCNE)	2232 s,	2223 s		2198 vs,	2180 vs		
Pd(PhNC)(PPh$_3$)(TCNE)	2220 (sh),	2213 ms,	2208 ms	2181 s			
Pd(PhNC)(AsPh$_3$)(TCNE)	2226 s,	2217 vs,	2212 vs	2182 vs			
Pd[P(O-i-Pr)$_3$]$_2$(TCNE)	2222 s,	2213 (sh)				1060 s (br) 768 ms	$\nu(P–O–C)_{as}$, $\nu(P–O–C)_{sym}$
Pd(Diphos)(TCNE)	2221 (sh)	2216 vs,	2208 vs				
[Rh(PhNC)$_2$(PPh$_3$)$_2$]Cl[d]				2122 vs			
Rh(PhNC)$_2$(PPh$_3$)(TCNE)Cl	2217 (sh)	2210 m		2195 s			
[Rh(PhNC)$_4$]Cl[d]				2177 m, 2134 vs,	2160 (sh), 2109 m		
Rh(PhNC)$_3$(TCNE)Cl	[e]			2211 vs,	2193 vs		
Rh(p-MeOC$_6$H$_4$NC)$_2$(CO)Cl				2160 vs,	2100 w	1998 vs, 307 s	1972 mw [ν(CO)], [ν(Rh–Cl)]
Rh(p-MeOC$_6$H$_4$NC)$_2$(TCNE)Cl	[e]			2210 s (br)			
Rh(p-MeOC$_6$H$_4$NC)$_2$(TCNE)(Py)Cl	2220 (sh)			2195 s (br)			

[a] Tetracyanoethylene vibration. [b] Isocyanide vibration. [c] Ref. 8. [d] In dichloromethane solution. [e] Masked by a broad isocyanide vibration.

The isocyanide ligands in (I) appear to be loosely bound to the metal. (I) reacts easily under ambient conditions with an excess of triphenylphosphine or -arsine in chloroform with replacement of one isocyanide molecule to give "mixed" derivatives of the type $Pd(PhNC)(EPh_3)(TCNE)$ [E = P, As; (II)]. These represent the first examples of transition metal cyanoolefin complexes containing mixed ligands. Treatment of (I) with a slight excess of triisopropylphosphite in dichloromethane leads to replacement of both isocyanide ligands giving the derivative $Pd[P(O\text{-}i\text{-}Pr)_3]_2(TCNE)$ (III), probably because of the better π-acceptor ability of this ligand. Furthermore, 1,2-bis(diphenylphosphino)ethane (Diphos) in equimolar amount reacts with (I) to replace both isocyanides, giving Pd(Diphos)(TCNE) (IV). The ease of replacement of coordinated isocyanides in (I) renders this complex a versatile intermediate for the preparation of novel cyanoolefin derivatives of palladium. On the other hand, the tetracyanoethylene–metal bond is highly stabilized, a feature which appears to be general for all the TCNE complexes prepared so far[1,2].

Rhodium derivatives

The ionic complex $[Rh(PhNC)_2(PPh_3)_2]Cl$[10] reacts with an equimolar amount of TCNE in dichloromethane with loss of one coordinated phosphine to give the neutral $Rh(PhNC)_2(PPh_3)(TCNE)Cl$ (V). $[Rh(PhNC)_4]Cl$[11] also reacts with TCNE (excess) with loss of one coordinated isocyanide to give the neutral $Rh(PhNC)_3(TCNE)Cl$ (VI). The isocyanide N≡C stretching frequency in (V) is some 70 cm^{-1} higher than that in the parent compound $[Rh(PhNC)_2(PPh_3)_2]Cl$. A similar increase in $\nu(N{\equiv}C)$ is observed in (VI). The shifts caused by coordination of TCNE again indicate a depletion of *d* electron density on the metal through extensive π back-bonding to the electronegative olefin. The $\nu(C{\equiv}N)$ of coordinated TCNE in (VI) could not be resolved from the overlapping absorptions due to the isocyanide $\nu(N{\equiv}C)$.

trans-$Rh(p\text{-}MeOC_6H_4NC)_2(CO)Cl$[11] reacts with an equimolar amount of TCNE in dichloromethane/benzene with an immediate change of color from red to violet followed by slow reversal to orange red. The final product is the neutral complex $Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)Cl$ (VII). This reaction probably takes place stepwise, involving initial formation of a labile adduct of TCNE with the starting complex, $Rh(p\text{-}MeOC_6H_4NC)_2(CO)(TCNE)Cl$, followed by loss of coordinated carbon monoxide. The coordinatively unsaturated nature of (VII) is shown by its ready reaction with an equimolar amount of pyridine in dichloromethane, which leads to the adduct $Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)(Pyridine)Cl$ (VIII). The isocyanide $\nu(N{\equiv}C)$ in both (VII) and (VIII) increases by some 50 cm^{-1} upon coordination of TCNE; the bands, however, are rather broad. The failure to isolate such an adduct as $Rh(p\text{-}MeOC_6H_4NC)_2(CO)(TCNE)Cl$ contrasts with the high stability of known adducts of TCNE with rhodium carbonyl complexes of type $Rh(EPh_3)_2(CO)(TCNE)Cl$[1] (E = P, As), and implies (*i*), that triarylphosphines or -arsines are better σ-donors than isocyanides, since they effectively stabilize the metal–carbonyl bond in the presence of electron-withdrawing ligands, and (*ii*) that isocyanides are stronger σ-donors and weaker π-acceptors than carbon monoxide.

In conclusion, isocyanides appear to be ligands particularly effective in reflecting electron density changes on the central metal caused by coordination of electron-withdrawing ligands.

EXPERIMENTAL

Materials

$Pd(PhNC)_2$ (black form) was prepared as described by Malatesta[5]. $[Rh(PhNC)_4]Cl$[11], $Rh(p\text{-}MeOC_6H_4NC)_2(CO)Cl$[10], and $[Rh(PPh_3)_2(PhNC)_2]Cl$[10] were prepared by literature methods.

Phenylisocyanide and *p*-methoxyphenylisocyanide were prepared by literature methods[12]. Tetracyanoethylene (Fluka) was purified by sublimation to give white crystals melting at 201–202°. All other chemicals were reagent grade and were used without further purification.

Preparation of Pd(PhNC)₂(TCNE)

1 mmole of $Pd(PhNC)_2$ suspended in 30 ml of chloroform was treated with stirring with 1 mmole of TCNE dissolved in 20 ml of benzene. After 1 h the suspension was refluxed for a few minutes. After filtration and concentration to a small volume under reduced pressure, addition of ethyl ether gave a pale yellow crystalline precipitate of $Pd(PhNC)_2(TCNE)$ (yield 90%).

Reactions of Pd(PhNC)₂(TCNE)

(*i*). *With triphenylphosphine.* 1 mmole of $Pd(PhNC)_2(TCNE)$ dissolved in 30 ml of chloroform was treated with an excess of triphenylphosphine (P/Pd = 3/1). After 30 min a mixture of ethyl ether/petroleum ether (b.p. 40–70°) (1/1 v/v) was added with stirring, whereupon pale yellow crystals of $Pd(PhNC)(PPh_3)(TCNE)$ were separated (yield 70%).

(*ii*). *With triphenylarsine.* The reaction was carried out in the same way as the above (As/Pd = 3/1). The yellow product $Pd(PhNC)(AsPh_3)(TCNE)$ was isolated by addition of ligroin (b.p. 90–110°) and evaporation of chloroform under reduced pressure (yield 70%).

(*iii*). *With triisopropylphosphite.* 1 mmole of $Pd(PhNC)_2(TCNE)$ suspended in 10 ml of dichloromethane was treated with a slight excess of triisopropylphosphite and the mixture was stirred for 4 h. After addition of 40 ml of ligroin, the whitish product $Pd[P(O\text{-}i\text{-}Pr)_3]_2(TCNE)$ was isolated by removal of the dichloromethane under reduced pressure and recrystallized from dichloromethane/ligroin (yield 65%).

(*iv*). *With 1,2-bis(diphenylphosphino)ethane.* 1 mmole of $Pd(PhNC)_2(TCNE)$ dissolved in 25 ml of chloroform was treated with an equimolar amount of diphosphine dissolved in ether. After 30 min the solution was concentrated to a small volume under reduced pressure and the pale yellow product Pd(Diphos)(TCNE) isolated by addition of a mixture of ethyl ether/petroleum ether (b.p. 40–70°, 1/1 v/v; yield 85%).

Reactions of tetracyanoethylene

(*i*). *With* $[Rh(PhNC)_2(PPh_3)_2]Cl$*.* 0.5 mmole of $[Rh(PhNC)_2(PPh_3)_2]Cl$ in 20 ml of dichloromethane was treated with 0.5 mmole of TCNE in 10 ml of benzene, which caused the orange-yellow colour of the solution to change to red. After concentration and addition of petroleum ether (b.p. 40–70°) the product $Rh(PhNC)_2(PPh_3)(TCNE)Cl$ was obtained as yellow-green crystals (yield 80%).

(*ii*). *With* $[Rh(PhNC)_4]Cl$*.* 1 mmole of $[Rh(PhNC)_4]Cl$ dissolved in dichloromethane/benzene (1/5 v/v) was treated dropwise with an excess of TCNE in 20 ml of benzene. The resulting dark green solution was concentrated to a small volume and ethyl ether was added, to give the olive-green product $Rh(PhNC)_3(TCNE)Cl$ as a finely-divided precipitate (yield 70%).

(iii). With trans-$Rh(p\text{-}MeOC_6H_4NC)_2(CO)Cl$. To 0.5 mmole of *trans*-$Rh(p\text{-}MeOC_6H_4NC)_2(CO)Cl$ in 20 ml of dichloromethane, TCNE (0.5 mmole) in 10 ml of benzene was added with stirring. The red solution immediately turned violet, then reverted gradually to orange-red. Concentration and addition of ethyl ether gave the product $Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)Cl$ as an orange-yellow solid (yield 80%).

Reaction of $Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)Cl$ *with pyridine*

0.34 mmole of $Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)Cl$ in 10 ml of dichloromethane was treated with 0.4 mmole of pyridine in 10 ml of dichloromethane with stirring. Concentration and addition of petroleum ether (b.p. 40–70°) gave $Rh(p\text{-}MeOC_6H_4NC)_2(TCNE)(Pyridine)Cl$ as a yellow precipitate.

Infrared spectra

IR spectra were recorded in the region 4000–250 cm^{-1} with a Perkin–Elmer 621 spectrophotometer. From 4000 to 1300 cm^{-1} hexachlorobutadiene mulls and NaCl plates were used; from 1700 to 250 cm^{-1} Nujol mulls and CsI plates were used. Solution spectra were recorded with KBr liquid cells of 1-mm path length. Calibration was performed against a polystyrene film. Accuracy is believed to be better than ± 2 cm^{-1}.

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