Tetramethylthiophen Complexes of Rhodium, Iridium, Palladium, and Ruthenium

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New tetramethylthiophen (tmt) complexes, $[M(\eta^5\text{-}C_5Me_5)(tmt)][PF_6]_2$ (M = Rh or Ir), $[Rh(diene)(tmt)][PF_6]$ (diene = cyclo-octa-1,5-diene or norbornadiene), $[Ru(p\text{-}cymene)(tmt)][PF_6]_2$, $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(tmt)_2][PF_6]$, and $[Pd(tmt)Cl_2]$ have been prepared; the Rh, Ir, and Ru complexes all contain η^5-bonded tmt but the two Pd complexes (which were only partially characterised) contain S- and, possibly, η^4-bonded tmt respectively. The 2,5-dimethylthiophen (dmt) complexes, $[Ir(\eta^5\text{-}C_5Me_5)(dmt)][PF_6]_2$ and $[Rh(cod)(dmt)][PF_6]$ were also prepared. The activity of these compounds as hydrogenation catalysts is discussed.

WE have reported in the preceding paper that thiophen has a drastic poisoning effect on the catalysis of olefin hydrogenation by di-μ-chloro-bis{(chloro)pentamethylcyclopentadienylrhodium} $[\{Rh(C_5Me_5)Cl_2\}_2]$, (1).[1] However, attempts to obtain a monomeric adduct of the type $[Rh(C_5Me_5)Cl_2L]$ (2; L = thiophen) met with no success and no evidence could be obtained for the existence of such a complex under normal conditions. This should be contrasted with the ease with which the chlorine-bridged dimer (1) is cleaved by tertiary phosphine or amine ligands to give adducts (2; L = R_3P, amine, *etc.*) [2] and also with the adducts that (1) forms with thioethers.[1] Thiophen did react with complex (1) under reducing conditions (Na_2CO_3–ethanol, 70 °C) to give a non-separable mixture of compounds. We therefore conclude that thiophen must act as a poison, not towards (1) itself, but towards the actual catalytic species that is formed from (1) under hydrogenation conditions.[3]

It was also not possible to obtain thiophen complexes by replacement of solvent in the tris-solvent species $[M(C_5Me_5)(sol)_3]^{2+}$ (3; M = Rh, Ir; sol = acetone and acetonitrile, *etc.*); such compounds have been very useful precursors for a variety of both of tris-complexes [1,4] and of π-bonded η^5- and η^6-complexes.[4,5]

By contrast, however, we found that 2,5-dimethylthiophen (dmt) and particularly 2,3,4,5-tetramethylthiophen (tmt) reacted with $[M(C_5Me_5)(sol)_3]^{2+}$ and formed π-complexes with other group VIII metal compounds.

Thiophen [6] and tmt complexes [7] of Cr^0, $[Cr(CO)_3(C_4R_4S)]$ (R = H or Me), are known and the crystal-structure determination of the former shows the thiophen to be η^5-bonded. The only other thiophen complexes that appear to have been reported are the cations $[Mn(C_4R_4S)(CO)_3]^+$ [8] and $[Fe(tmt)_2]^{2+}$;[9] the tmt ligands are also presumed to be η^5-bonded in each case and a direct analogy to the cyclopentadienyl complexes, $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ and $[Fe(\eta^5\text{-}C_5H_5)_2]$, may be drawn.

RESULTS AND DISCUSSION

Rhodium and Iridium Complexes.—Both the rhodium and the iridium tris-acetone species (3) reacted with tmt

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[1] M. J. H. Russell, C. White, and P. M. Maitlis, *J.C.S. Dalton*, preceding paper.

[2] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1969, **91**, 5970.

[3] D. S. Gill, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1978, 617.

[4] C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Dalton*, 1977, 1654.

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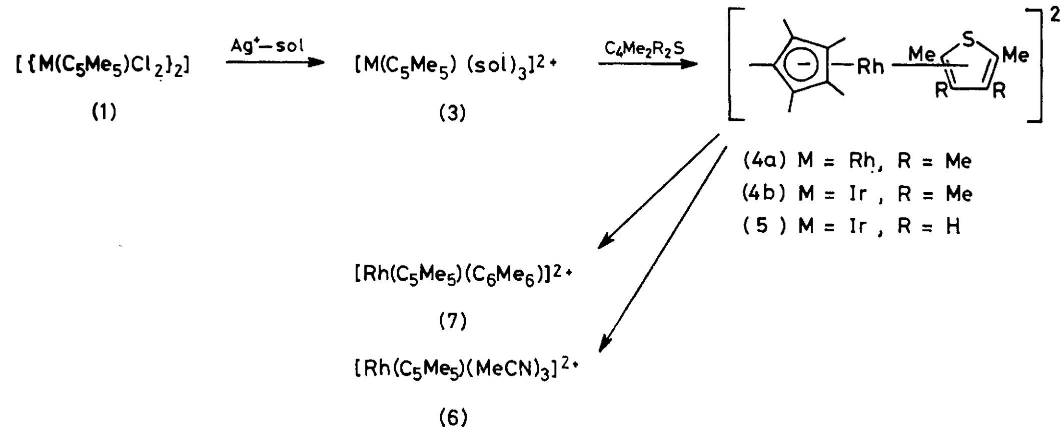
[7] R. Guilard, J. Tirouflet, and P. Fournari, *J. Organometallic Chem.*, 1971, **33**, 195.

[8] H. Singer, *J. Organometallic Chem.*, 1967, **9**, 135.

[9] D. M. Braitsch and R. Kumarappan, *J. Organometallic Chem.*, 1975, **84**, C37.

to give $[M(C_5Me_5)(tmt)][PF_6]_2$ (4a) and (4b), and dmt reacted with the iridium tris-solvent species (3b) to give (5). No thiophen complexes could be isolated, nor was it possible to obtain the Rh–dmt complex analogous to (5). There is an exact parallel between these reactions and the relative stability towards displacement of benzene and methylbenzenes in $[M(C_5Me_5)(arene)]^{2+}$ by solvents.[4] In that case it was found that the more heavily methylated the benzene, the more stable was the complex; thus benzene in $[Rh(C_5Me_5)(benzene)]^{2+}$ was rapidly displaced by acetone whereas *p*-xylene in $[Rh(C_5Me_5)(p\text{-xylene})]^{2+}$ was displaced by dimethyl sulphoxide but that complex was much more stable in acetone. Furthermore, the iridium analogues were more stable than the rhodium complexes, for example, benzene in $[Ir(C_5Me_5)(benzene)]^{2+}$ was not displaced by either acetone or dimethyl sulphoxide.



In principle, thiophens can π-bond in either an η^4- (all sp^2 C-atoms bonded) or η^5- (all sp^2-C and the S-atom bonded) fashion. While definite proof for the mode of binding can only be obtained from a crystal structure determination, tmt and dmt appear to be η^5-bonded in (4) and (5). The n.m.r. spectra are consistent with this and if the thiophens were η^4-bonded then it should be possible to introduce a further small ligand (or solvent molecule) at the metal without loss of the thiophen. None of these complexes contain, for example, acetone from reactions with (3; sol = acetone) and attempts to introduce acetonitrile to give $[Rh(C_5Me_5)(C_4Me_4S)(MeCN)]^{2+}$ failed; under forcing conditions the tmt was completely replaced by acetonitrile to give (6). We therefore conclude that both the C_5Me_5 and the tmt are acting as tridentate ligands and that the latter is also η^5-bonded.

$$[Rh(diene)(C_4Me_2R_2S)]^+ + Me_2CO \rightleftharpoons [Rh(diene)(Me_2CO)_2]^+ + C_4Me_2R_2S$$

In addition to its displacement by acetonitrile from (4a) tmt was also replaced by hexamethylbenzene in acetone to give (7).[10]

Cationic complexes of Rh^I, (8), were prepared by reaction of the $[\{Rh(diene)Cl\}_2]$ [diene = cyclo-octa-1,5-diene (cod), or norbornadiene (nbd)] with dmt or tmt in the presence of $AgPF_6$.

The norbornadiene complex (8) was not appreciably dissociated in acetone and showed the expected n.m.r. spectra. From the ^{13}C spectrum it was evident that the asymmetry demanded by a rigidly square planar structure (with the two tmt double bonds co-ordinated) was absent and therefore we presume that there is either free rotation about the Rh–tmt axis or that a fast exchange process is occurring.

$$[\{Rh(diene)Cl\}_2] + C_4Me_2R_2S \xrightarrow{AgPF_6} [Rh(C_4Me_2R_2S)(diene)][PF_6]$$

(8a) diene = cod, R = Me
(8b) diene = nbd, R = Me
(8c) diene = cod, R = H

The cyclo-octadiene complex (8a) by contrast showed evidence of dissociation to the extent of some 15% in acetone solution. Peaks at δ 79.1 [J(C–Rh) = 12.2] and 31.0 in the ^{13}C spectrum are assigned to $[Rh(cod)(Me_2CO)_2]^+$ and at δ 1.94, 2.22 in the ^1H spectrum to free dmt. In dichloromethane no such dissociation occurred and the ^{13}C spectrum was again consistent with the expected structure, and with that for (8b).

The cod–dmt complex (8c) was 85 ± 5% dissociated in acetone; resonances in the ^1H and the ^{13}C spectrum due to free dmt and to $[Rh(cod)(Me_2CO)_2]^+$ were strong and only weak ones were observed which could be assigned to (8c).

Ruthenium-p-*Cymene–tmt Complex*.—When di-μ-chloro-bis[chloro(*p*-cymene)ruthenium(II)] (9)[11] was treated with tmt in the presence of $AgPF_6$, the tmt–ruthenium dicationic complex (10), analogous to complexes (4) and (5), was obtained.

The analytical and spectroscopic data are quite consistent with the structure proposed and the observed equivalence of the isopropyl methyl groups and of the

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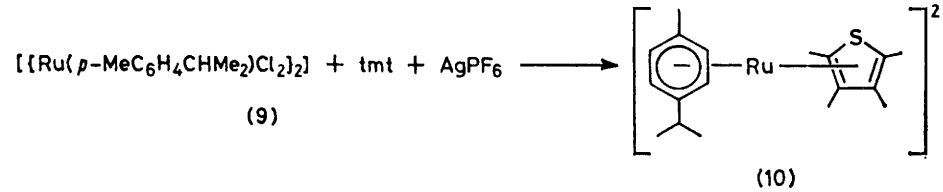
[11] M. A. Bennett and A. K. Smith, *J.C.S. Dalton*, 1974, 233.

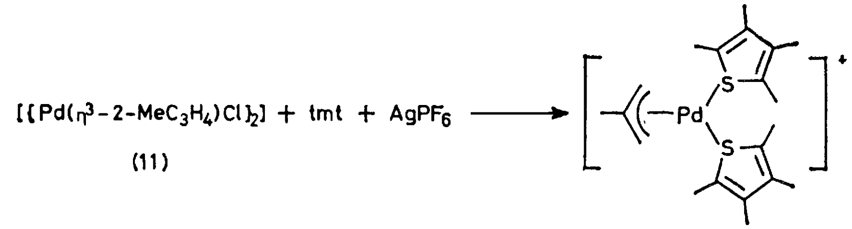
thiophen methyls at C(2) and C(5), and C(3) and C(4) suggest that either free rotation about the ring–metal bonds is occurring or that the molecule has a plane of symmetry and is rigid in solution.


(9)

(10)

Attempts to prepare [{$Ru(tmt)Cl_2$}$_2$] by replacement of *p*-cymene by tmt failed.

Palladium–tmt Complexes.—Reaction of di-μ-chloro-bis(2-methylallylpalladium) (11) with tmt in the presence of $AgPF_6$ gave a brown oil; all attempts to crystallise it led to decomposition. The ^1H and the ^{13}C n.m.r. spectra of the oil showed the resonances of the co-ordinated tmt to be very close to those of tmt itself and integration of the ^1H spectrum suggested there to be two tmt molecules per methylallylpalladium fragment. On this basis we propose an S-bonded structure for this complex (12). The spectrum in acetone remained unchanged down to −60 °C.


(11)

(12)

Reaction of dichlorobis(benzonitrile)palladium with tmt gave, after purification, a brown complex (13) the analysis for which was consistent with the molecular formula [$Pd(tmt)Cl_2$] and which showed bands indicative of terminal Pd–Cl bonds at 360s, 340s, 304m, and 292s cm^{-1} in its far-i.r. spectrum. This complex was quite insoluble in all but strongly co-ordinating solvents in which displacement of tmt occurred. However, when the compound was freshly precipitated from solution it contained benzonitrile (in varying amounts) and was sufficiently soluble for n.m.r. studies. Apart from the benzonitrile absorptions two resonances due to the two types of tmt methyl groups were observed in both the ^1H and the ^{13}C spectrum, while the tmt ring carbons appeared at δ 109.0 and 111.9 in the ^{13}C spectrum at lower frequency than free tmt. In view of this we tentatively suggest the complex to contain η^4-bonded tmt.

dmt and tmt Complexes as Hydrogenation Catalysts.—By comparison with complex (1), which shows high activity as an olefin hydrogenation catalyst at 20 °C and 1 atm H_2,[3] the complex (4a) has appreciably lower activity. However, complexes (4a), (4b), and (5) all showed substantial catalytic activity for cyclohexene hydrogenation at 50 °C and 50 atm H_2 without metal being formed; interestingly, while hydrogenation by complex (1) is strongly co-catalysed by base this was not the case for (4a) and (5), both of which showed markedly greater activity in the *absence* of triethylamine.

The rhodium(I) complexes (8a—c) and the palladium(II) complex (13) were also active catalysts but rapidly deposited metal. Complex (5) was also very active for the hydrogenation of hex-1-ene and styrene and in the latter case some reduction of the aromatic ring, to give ethylcyclohexane, also occurred. By comparison, [$Cr(tmt)(CO)_3$][7] showed no activity for cyclohexene hydrogenation under these conditions.

EXPERIMENTAL

Typical preparations are detailed below; microanalytical, n.m.r. and hydrogenation data are summarised in Tables 1, 2, and 3 respectively.

TABLE 1

Microanalytical data [a]

Complex	% Composition C	H	S	Yield (%)
[$Rh(C_5Me_5)(tmt)$][PF_6]$_2$ (4a)	32.0	4.0	5.0	88 [d]
	(32.3)	(4.1)	(4.8)	
[$Ir(C_5Me_5)(tmt)$][PF_6]$_2$ (4b)	28.6	3.7	4.7	70 [e]
	(28.5)	(3.6)	(4.2)	
[$Ir(C_5Me_5)(dmt)$][PF_6]$_2$ (5)	26.5	3.3	5.5	69 [e]
	(26.3)	(3.2)	(4.4)	
[Rh(cod)(tmt)][PF_6] (8a)	38.6	5.0	7.0	85 [f]
	(38.7)	(4.9)	(6.5)	
[Rh(cod)(dmt)][PF_6] (8c)	36.1	4.4	7.0	97 [f]
	(35.9)	(4.3)	(6.8)	
[Rh(nbd)(tmt)][PF_6] (8b)	37.1	4.1	7.1	73 [g]
	(37.5)	(4.2)	(6.7)	
[$PdCl_2(tmt)$] [b,c] (13)	30.3	4.0	10.7	99
	(30.3)	(3.8)	(10.1)	
[Ru(*p*-cymene)(tmt)][PF_6]$_2$ (11)	32.9	4.1	6.6	99 [h]
	(32.5)	(3.9)	(4.8)	

[a] Calculated values in parentheses. [b] Cl, 22.5 (22.3%). [c] Insoluble material after purification by reprecipitation. [d] Prepared by method (i). [e] Prepared by method (ii). [f] Prepared by method (ii) from [{Rh(cod)Cl}$_2$]. [g] Prepared by method (ii) from [{Rh(nbd)Cl}$_2$]. [h] Prepared by method (ii) from [{Ru(*p*-cymene)Cl_2}$_2$].[11]

Method (*i*).—[$Rh(C_5Me_5)(C_4Me_4S)$][PF_6]$_2$ (4a). Tetramethylthiophen (0.15 ml) was added to a solution of

$[\mathrm{Rh(C_5Me_5)(NCMe)_3][PF_6]_2}$ (0.2 g, 0.3 mmol) in acetone (5 ml). The solution was stirred for 5 min and then diethyl ether was added to give an off-white precipitate, which was crystallised from acetone–diethyl ether to give a cream microcrystalline compound (4a) (0.18 g, 88%).

TABLE 2

N.m.r. spectra (in $[^2\mathrm{H}_6]$acetone)

Compound	^{1}H N.m.r. spectra (δ): $\mathrm{C_4}\mathit{Me}_4\mathrm{S}$	$\mathrm{C_5}\mathit{Me}_5$	Other	
$\mathrm{C_4Me_4S}$ (tmt) [a]	1.96, 2.25			
$[\mathrm{Rh(C_5Me_5)(tmt)][PF_6]_2}$ (4a)	2.40, 2.62	2.21		
$[\mathrm{Ir(C_5Me_5)(tmt)][PF_6]_2}$ (4b)	2.46, 2.58	2.30		
$[\mathrm{Rh(cod)(tmt)][PF_6]}$ (8a)	2.04, 2.42		$\mathrm{CH_2}$ CH	2.35 4.30 (bd)
$[\mathrm{Rh(nbd)(tmt)][PF_6]}$ (8b)	2.00, 2.45		$\mathrm{CH_2}$ CH(sp^3) CH(sp^2)	1.23 3.32 or 3.68 (bd) 4.13 (bd)
$[\mathrm{Ru}(p\text{-cymene})(\mathrm{tmt})][\mathrm{PF_6}]_2$ (10)	2.52, 2.58		$\mathit{Me}\mathrm{C_6H_4Pr^i}$ $\mathrm{MeC_6H_4}\mathit{Pr}^\mathrm{i}$ $\mathrm{MeC_6}\mathit{H}_4\mathrm{Pr^i}$	2.58 1.44 (d, J_{HH} = 7) 3.15 (m) 6.83 (m)
$[\mathrm{Pd}(\eta^3\text{-2-MeC_3H_4})(\mathrm{tmt})_2][\mathrm{PF_6}]$ (12)	1.99, 2.26		$\mathit{Me}\mathrm{C_3H_4}$ *anti*-$\mathrm{CH_2}$ *syn*-$\mathrm{CH_2}$	2.13 3.29 4.03
$[\mathrm{Pd(tmt)Cl_2}]$ [a,c] (13)	1.90, 2.36			
$[\mathrm{Cr(tmt)(CO)_3}]$ [a,d]	2.15			
	$\mathrm{C_4}\mathit{Me}_2\mathrm{H_2S}$	$\mathrm{C_4Me_2}\mathit{H}_2\mathrm{S}$	Other	
$\overline{\mathrm{S{\cdot}CMe{:}CH{\cdot}CH{:}C}}\mathrm{Me}$ (dmt) [a]	2.41	6.55		
$[\mathrm{Ir(C_5Me_5)(dmt)][PF_6]_2}$ (5)	2.82	7.42	$\mathrm{C_5}\mathit{Me}_5$	2.49
$[\mathrm{Rh(cod)(dmt)][PF_6]}$	2.10	7.02	$\mathrm{CH_2}$ CH	*e* 4.66 (bd)

Compound	^{13}C N.m.r. spectra (δ) [J(C–Rh) in parentheses in Hz]: $\mathrm{C_4}\mathit{Me}_4\mathrm{S}$	$\mathit{C}_4\mathrm{Me_4S}$	$\mathrm{C_5}\mathit{Me}_5$	$\mathit{C}_5\mathrm{Me_5}$	Other	
$\mathrm{C_4Me_4S}$ (tmt) [a]	12.6, 12.9	127.7, 132.9				
$[\mathrm{Rh(C_5Me_5)(tmt)][PF_6]_2}$ (4a)	10.6, 12.2	118.6, 122.0 (7.6) (4.5)	9.3	110.6 (6.6)		
$[\mathrm{Ir(C_5Me_5)(tmt)][PF_6]_2}$ (4b)	10.3, 11.8	114.8, 107.3	8.8	104.2		
$[\mathrm{Rh(cod)(tmt)][PF_6]}$ (8a)	12.1, 12.3 [b]	103.5, 122.4 [b] (4.6) (3.1)			$\mathrm{CH_2}$ CH	31.7 [b] 85.1 (12.2)
$[\mathrm{Rh(nbd)(tmt)][PF_6]}$ (8b)	12.4, 12.8	103.2, 121.2 (3.1) (4.2)			$\mathrm{CH_2}$ CH(sp^3) CH(sp^2)	49.0 54.4 (9.2) 60.4 (6.1)
$[\mathrm{Ru}(p\text{-cymene})(\mathrm{tmt})][\mathrm{PF_6}]_2$ (10)	12.2, 13.7	107.9, 113.9			$\mathit{Me}\mathrm{C_6H_4Pr^i}$ $\mathrm{MeC_6H_4}\mathit{Pr}^\mathrm{i}$ $\mathrm{Me}\mathit{C}_6\mathrm{H_4Pr^i}$	18.0 22.9, 32.0 92.6, 95.2, 110.9, 121.3
$[\mathrm{Pd}(\eta^3\text{-2-MeC_3H_4})(\mathrm{tmt})_2][\mathrm{PF_6}]$ (12)	12.8. 13.0	128.7, 133.1			$\mathit{Me}\mathrm{C_3H_4}$ C(1) C(2)	22.6 64.1 135.4
$[\mathrm{Pd(tmt)Cl_2}]$ [a,c] (13)	13.3, 13.9	119.1, 122.8				
$[\mathrm{Cr(tmt)(CO)_3}]$ [a,d]	13.2, 14.2	100.3, 100.7				
	$\mathrm{C_4}\mathit{Me}_2\mathrm{H_2S}$	C(2)	C(3)		Other	
$\overline{\mathrm{S{\cdot}\underset{2}{C}Me{:}CH{\cdot}\underset{3}{C}H{:}C}}\mathrm{Me}$ (dmt) [a]	15.2	124.7	137.2			
$[\mathrm{Ir(C_5Me_5)(dmt)][PF_6]_2}$ (5)	13.3	105.3	112.7		$\mathrm{C_5}\mathit{Me}_5$ $\mathit{C}_5\mathrm{Me_5}$	9.6 99.9
$[\mathrm{Rh(cod)(dmt)][PF_6]}$	13.2	108.2 (1.5)	*e*		$\mathrm{CH_2}$ CH	30.6 83.1 (12.2)

[a] In $\mathrm{CDCl_3}$. [b] In $\mathrm{CH_2Cl_2}$. [c] This sample contains benzonitrile. [d] See ref. 7. [e] Not assigned.

$[\mathrm{Rh(C_5Me_5)(MeCN)_3][PF_6]_2}$ (6). $[\mathrm{Rh(C_5Me_5)(C_4Me_4S)}][\mathrm{PF_6}]_2$ (0.3 g, 0.45 mmol) was refluxed in acetonitrile (10 ml) for 16 h. The solution was evaporated to dryness under reduced pressure. Crystallisation of the residue from acetone–diethyl ether gave complex (6) as yellow crystals (0.20 g, 68%). The ^{1}H n.m.r. and i.r. spectra were identical to those reported.[4]

$[\mathrm{Rh(C_5Me_5)(C_6Me_6)][PF_6]_2}$ (7). $[\mathrm{Rh(C_5Me_5)(tmt)][PF_6]_2}$ (0.40 g, 0.60 mmol) and hexamethylbenzene (0.10 g, 0.62 mmol) were refluxed in acetone (10 ml) for 16 h. The solvent was removed under reduced pressure; crystallisation of the residue from acetone–diethyl ether gave complex (7) as white crystals (0.31 g, 80%). The ^{1}H n.m.r. and i.r. spectra were identical to those reported.[10]

Method (*ii*).—$[\mathrm{Ir(C_5Me_5)(tmt)][PF_6]_2}$ (4b). Silver hexafluorophosphate (0.51 g, 2 mmol) in acetone (5 ml) was added to a solution of $[\mathrm{Ir_2(C_5Me_5)_2Cl_4}]$ (0.40 g, 0.5 mmol) and tetramethylthiophen (0.5 ml) in acetone (5 ml). The mixture was stirred for 10 min, and then filtered through What-

TABLE 3

Catalysts for the hydrogenation of cyclohexene [a]

Complex	% Cyclohexane formed Base present	 Base absent
$[Rh(C_5Me_5)(tmt)][PF_6]_2$ (4a)	33	87
$[Ir(C_5Me_5)(tmt)][PF_6]_2$ (4b)	40	15
$[Ir(C_5Me_5)(dmt)][PF_6]_2$ (5)	45	98
$[Rh(cod)(tmt)][PF_6]$ (8a)	94 [b]	100 [b]
$[Rh(cod)(dmt)][PF_6]$ (8c)	100 [b]	96 [b]
$[Rh(nbd)(tmt)][PF_6]$ (8b)	98 [b]	0
$[PdCl_2(tmt)]$ (13)	70 [b]	99 [b]
$[Ru(p\text{-cymene})(tmt)][PF_6]_2$ (11)	20	42
$[Cr(CO)_3(tmt)]$ [7]	0	0

[a] 0.05 mmol of catalyst, cyclohexene (2 ml, 20 mmol), propan-2-ol (18 ml) at 50 bar hydrogen, 50 °C over 24 h. The added base was Et_3N (0.2 ml, 1.5 mmol). [b] Decomposition to metal.

man 545 paper; the filtrate was taken to dryness under reduced pressure. Crystallisation of the residue from acetone–diethyl ether gave off-white crystals of complex (4b) (0.53 g, 70%).

$[Pd(tmt)Cl_2]$ (13). Tetramethylthiophen (0.4 ml) was added to a solution of bis(benzonitrile)dichloropalladium (0.75 g) in toluene (25 ml). The solution went dark immediately and gave a small amount of a brown precipitate. The mixture was stirred for 1 h at 20 °C, after which the precipitate (38 mg) was filtered off and the volume of the filtrate reduced (to 8 ml); diethyl ether (8 ml) was added to it to give a red-brown precipitate (0.33 g) which was filtered off and was shown to contain both co-ordinated benzonitrile and tetramethylthiophen. This could be purified from benzonitrile by dissolving it in dichloromethane and re-precipitating it with ether; it became progressively darker in colour and more insoluble.

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