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Synthesis and properties of new tris(cyanoethyl)phosphine complexes of platinum (0,II), palladium (0,II), iridium (I) and rhodium (I). Conformational analysis of tris(cyanoethyl)phosphine ligands [1]

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Abstract

The tris(cyanoethyl)phosphine (tcep) complexes *trans*-[$PtCl_2(tcep)_2$], *cis*-[$PtMe_2(tcep)_2$], and *trans*-[$PtMeCl(tcep)_2$] are prepared by treatment of the corresponding [PtXY(cod)] (cod = 1,5-cyclooctadiene) with tcep. Reduction of *trans*-[$PtCl_2(tcep)_2$] with $NaBH_4$ gives *trans*-[$PtHCl(tcep)_2$] which, in the presence of tcep and NEt_3, gives the coordinatively unsaturated platinum(0) complex [$Pt(tcep)_3$]. This coordinatively unsaturated species is also formed when [$Pt(norbornene)_3$] reacts with tcep. [$Pt(tcep)_3$] is very unreactive compared to its PEt_3 analogue: it is air-stable and does not react with further tcep to form an 18-electron species. It is protonated by $HBF_4 \cdot OEt_2$ to form [$PtH(tcep)_3$]BF_4. The complex *trans*-[$PdCl_2(tcep)_2$] is made from [$PdCl_2(NCPh)_2$] and tcep and the derivatives *trans*-[$PdX_2(tcep)_2$] (X = Br or I) are made by metathesis of the dichloro complex. Reduction of *trans*-[$PdCl_2(tcep)_2$] with LiOMe in the presence of tcep gave the palladium(0) complex [$Pd(tcep)_3$] which, like its platinum(0) analogue, undergoes exchange with free tcep on the NMR timescale. The palladium complex reacts with dibenzylideneacetone (dba) to form [$Pd(\eta^2\text{-dba})(tcep)_2$]; the same product is formed in the reaction of [$Pd(\eta^2\text{-dba})_2$] and tcep. Reaction of [$Pd_2Cl_2(\eta^3\text{-}C_3H_3)_2$] and tcep gives [$PdCl(tcep)(\eta^3\text{-}C_3H_3)$] or [$Pd(tcep)_2(\eta^3\text{-}C_3H_3)$]Cl depending on stoichiometry. The rhodium(I) and iridium(I) complexes *trans*-[$MCl(CO)(tcep)_2$], [MCl(tcep)(cod)] and [$MCl(tcep)_3$] are all readily made from tcep and an appropriate precursor. All new compounds have been fully characterised by a combination of elemental analysis, IR, ^{31}P, ^{13}C, ^{1}H and ^{195}Pt NMR spectroscopy. The crystal structure of [$IrCl(tcep)_3$] as a MeCN solvate shows a distorted square planar coordination geometry (*trans* angles at Ir(I) ca. 164°, *cis* P–Ir–P av. 96°, *cis* P–Ir–Cl av. 85°). Analysis of the conformations of tcep ligands in this and other published tcep complexes shows there is a preference for conformations in which aaa, aag or g^+g^- (a = anti, g = gauche) arrangements of the three M–P–C–C chains are avoided. © 1998 Elsevier Science S.A.

Keywords: Platinum; Palladium; Rhodium; Iridium; Tris(cyanoethyl)phosphine; Synthesis; Structure; Conformation

1. Introduction

Tris(cyanoethyl)phosphine (tcep) is produced in tonne-quantities per annum mainly for use in the photographic industry [1–4] and is thus readily available commercially. The presence of the β-cyano groups makes tcep very different from other small trialkylphosphines: tcep is an air-stable solid (m.p. + 97°C) of low basicity (pK_a 1.37) while tri-*n*-propylphosphine is a very air-sensitive liquid (m.p. − 83°C) of high basicity (pK_a 8.64) [5,6]. The coordination chemistry of tcep is also sharply different from other trialkyl phosphines: spectroscopic, structural and theoretical studies [7–13] indicate that tcep has a π-acceptor capacity similar to $P(OPh)_3$ and though Tolman predicted [7] the cone-angle for tcep to be ca. 132°, recently Liu et al. [14] have shown by crystallography that tcep can have a much larger cone angle of 175°.

In this paper we report the synthesis and chemistry of some new platinum, palladium, rhodium and iridium complexes with tcep which we wanted to screen as catalyst precursors for hydrophosphination of acrylonitrile [15]. The conformations of coordinated tcep are analysed in detail. Previously, other groups have reported aspects of tcep coordination chemistry with platinum [16–25], palladium [25,26] and rhodium [27] and a preliminary account of some of this work has been given [15].

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[1] Dedicated to Professor Ken Wade on the occasion of his 65th birthday.

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2. Results and discussion

Tris(cyanoethyl)phosphine (tcep) can be conveniently made on a large scale by treatment of $[P(CH_2OH)_4]Cl$ with NaOH in the presence of acrylonitrile [28–30] or is commercially available.

2.1. Platinum complexes of tris(cyanoethyl)phosphine

The platinum chemistry with tcep is summarised in Scheme 1 and the characterising data are given in Tables 1–3.

The dichloroplatinum complex **1** has been previously reported [16–18]. Treatment of $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) with tcep gives exclusively the *trans* complex **1** under conditions that many other PR_3 ligands (e.g., PMe_3, PEt_3, PBu^n_3, PPh_3) would give the *cis* isomer; in this reaction tcep behaves like a bulky PR_3 ligand [31]. The crystal structure of **1** does indeed show that the effective cone angle of the tcep in this complex is ca. 160° [18].

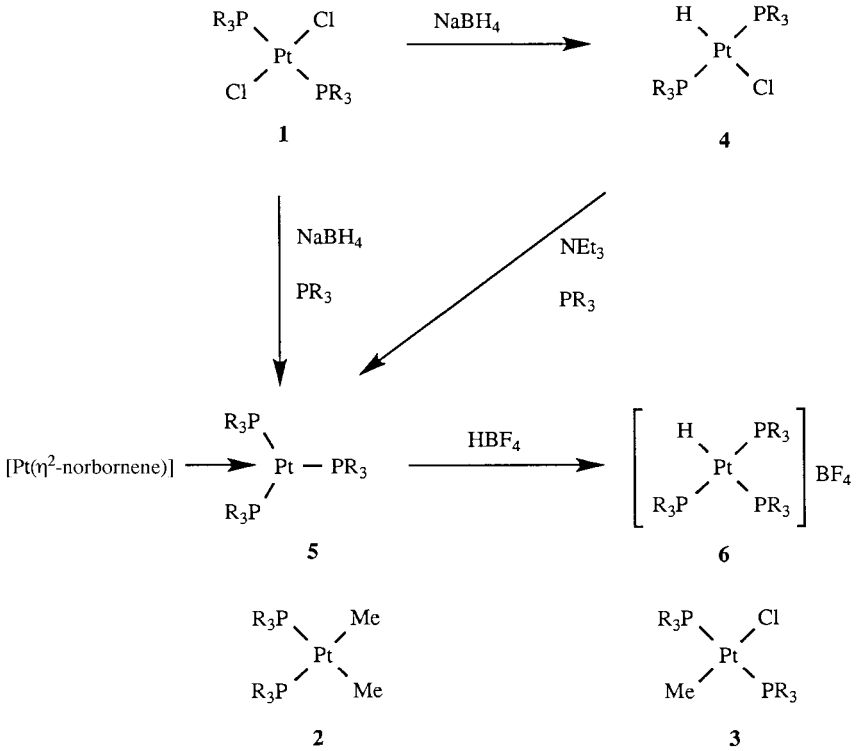
Treatment of $[PtMe_2(cod)]$ with tcep gives the expected *cis*-$[PtMe_2(tcep)_2]$ (**2**). The complex *trans*-$[PtMeCl(tcep)_2]$ (**3**) was made by addition of tcep to [PtMeCl(cod)]; the formation of the *trans* isomer **3** is typical of tertiary phosphines [32,33] but contrasts with the *cis* preference of $P(OR)_3$ ligands [34] with which tcep has been compared [7–13].

The sparingly soluble hydridoplatinum(II) complex **4** is obtained by treatment of **1** with $NaBH_4$ in MeCN and has been characterised by elemental analysis, ^{31}P, ^{13}C NMR spectroscopy and especially (i) the IR spectrum (nujol mull) which had bands at 2245 cm^{-1} for ν(PtH), 2203 cm^{-1} for ν(CN) and 285 cm^{-1} for ν(PtCl), and (ii) the ^1H NMR spectrum which showed a hydride resonance at $\delta - 17.05$, a triplet with ^{195}Pt satellites (^2J(HP) 14.8 Hz, ^1J(HPt) 1244 Hz).

Table 1
Elemental analyses[a]

	C	H	N
2	38.70 (39.30)	5.05 (4.95)	13.75 (13.75)
3	36.15 (36.15)	4.40 (4.30)	13.00 (13.30)
4	35.00 (35.00)	4.10 (4.10)	13.05 (13.60)
5	41.85 (41.65)	4.70 (4.75)	16.30 (16.10)
6[b]	36.45 (36.10)	4.35 (4.10)	13.84 (14.05)
7a	38.05 (38.35)	4.55 (4.30)	14.60 (14.90)
7b	33.35 (33.10)	4.00 (3.70)	12.40 (12.85)
7c	28.90 (28.95)	3.45 (3.25)	10.85 (11.25)
8	46.55 (47.25)	5.40 (5.25)	17.65 (18.35)
9	56.85 (57.70)	5.30 (5.40)	11.55 (11.40)
10	38.45 (38.30)	4.55 (4.55)	11.25 (11.15)
11	44.60 (44.30)	5.30 (5.15)	14.10 (14.75)
12[c]	42.20 (42.10)	4.80 (4.60)	14.80 (14.40)
13[d]	35.70 (35.55)	3.90 (3.80)	12.90 (13.10)
14	46.10 (46.40)	5.70 (5.50)	9.05 (9.55)
15	38.35 (38.60)	4.75 (4.60)	7.65 (7.95)
16[e]	40.60 (40.25)	4.60 (4.55)	16.10 (16.10)

[a] Calculated values in parentheses.
[b] Contains $2H_2O$, as shown by ^1H NMR spectroscopy.
[c] Contains 0.5 Me_2CO, as shown by ^1H NMR spectroscopy. Cl analysis 6.90 (6.40).
[d] Cl analysis 5.75 (5.30).
[e] Contains 0.5 MeCN as shown by X-ray crystallography.



Scheme 1. Platinum chemistry with tcep (R = CH_2CH_2CN).

Table 2
^{31}P and ^{195}Pt NMR data[a]

	Solvent	δ(P)[b]	^1J(MP)	δ(Pt)
tcep	$(CD_3)_2SO$	−24.0		
1	$(CD_3)_2SO$	10.4	2483	
2	$(CD_3)_2CO$	13.1	1814	−151
3	$(CD_3)_2CO$	15.8	2942	7
4	CD_3CN	22.9	2808	−475
5	$(CD_3)_2CO$	38.9	4236	17[c]
6	$(CD_3)_2SO$	8.3 (22)	2585	−570
		7.3	2100	
7a	$(CD_3)_2SO$	14.9		
7b	$(CD_3)_2SO$	12.3		
7c	$(CD_3)_2SO$	5.9		
8	CD_3CN	7.2		
9	$(CD_3)_2SO$	13.7 (15)		
		10.7		
10	$(CD_3)_2CO$	19.5		
11	$(CD_3)_2SO$	12.4		
12	$(CD_3)_2CO$	22.2	120	
13	$(CD_3)_2CO$	18.2		
14	$(CD_3)_2CO$	21.3	154	
15	$(CD_3)_2CO$	9.8		
16	$(CD_3)_2SO$	33.4 (41)	181	
		17.6	134	
17	$(CD_3)_2SO$	9.6 (22)		
		−1.3		

[a] ^{31}P NMR spectra (36.2 MHz) measured at 28°C with chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz (±3). ^{195}Pt NMR spectra (19.2 MHz) measured at 28°C with chemical shifts (δ) in ppm (±0.5) to high frequency of Ξ(Pt) 21.4 MHz.
[b] Value in parentheses is ^2J(PP).
[c] In $(CD_3)_2SO$.

Reductive elimination of HCl from **4** is effected by treatment with NEt_3 in the presence of tcep to give [Pt(tcep)$_3$] (**5**). The platinum(0) complex **5** can also be prepared by treatment of [Pt(η^2-norbornene)$_3$] with 3 equivalents of tcep or by reduction of *trans*-[$PtCl_2$(tcep)$_2$] with $NaBH_4$ in the presence of tcep (see Scheme 1). The assignment of the three-coordination of the platinum in **5** is based on elemental analysis, ^{1}H, ^{13}C, ^{31}P and especially ^{195}Pt NMR spectroscopy: the ^{195}Pt NMR signal for **5** is a quartet with ^1J(PtP) of 4236 Hz, similar to the ^1J(PtP) of 4188 Hz for [Pt(PEt_3)$_3$] and quite different from the ^1J(PtP) of 3727 Hz for [Pt(PEt_3)$_4$] [35]. The IR spectrum of **5** showed a single ν(CN) at 2250 cm^{-1} consistent with the absence of coordinated cyano groups [36].

The coordinatively unsaturated complex **5** shows no tendency to bind a fourth tcep ligand: treatment of **5** with 10 equivalents of tcep results in broadened ^{31}P NMR resonances for **5** and tcep (see Fig. 1) but no change in δ(P) or ^1J(PtP), consistent with slow phosphine exchange on the NMR timescale, presumably via the transient 18-electron species [Pt(tcep)$_4$]. Complex **5** is soluble in acetone, acetonitrile and dmso but insoluble in other common organic solvents (e.g. CH_2Cl_2, toluene), it is not protonated by MeOH or H_2O and decomposes only very slowly in air even in solution. These properties of **5** may be contrasted with those of the extremely air-sensitive analogue [Pt(PEt_3)$_3$] which forms [Pt(PEt_3)$_4$] in the presence of PEt_3, is soluble in most common organic solvents and reacts with methanol or water to give [PtH(PEt_3)$_3$]$^+$ [37].

The platinum(0) complex **5** can be protonated by HBF_4 in diethyl ether to give [PtH(tcep)$_3$]BF_4 (**6**) (see Tables 1–3 for the data).

2.2. Palladium complexes of tris(cyanoethyl)phosphine

The palladium chemistry is summarised in Scheme 2 and characterising data are given in Tables 1–3. The

Table 3
^{13}C NMR data[a]

	Solvent	*C*N[b]	P*C*H$_2$[b]	PCH$_2$*C*H$_2$[b]	Other[b]
tcep	$(CD_3)_2SO$	120.8 (10.8)	20.6 (15.1)	13.3 (19.4)	
2	$(CD_3)_2SO$	119.5[c]	20.0[c]	12.9 (29.1)[d]	δ(CH_3) 4.0 (109, 591)[e]
3	$(CD_3)_2SO$	119.4 (15.4)	17.8	12.1 (32.1)[d]	δ(CH_3) -22.1 (6, 645)[e]
4	CD_3CN	120.3 (8.0)	21.1[c]	14.1 (39.2)[d]	
7a	$(CD_3)_2SO$	119.9 (15.1)	17.4 (27.5)	11.9	
7b	$(CD_3)_2SO$	119.8 (15.1)	19.0 (27.5)	12.2	
7c	$(CD_3)_2SO$	119.4 (17.9)	23.0 (30.3)	12.9	
10	$(CD_3)_2CO$	119.5 (16.2)	21.0 (22.6)	12.9 (5.4)	δ(C_3H_5)79.6 (32.3), 118.3 (5.4), 54.6.
11[f]	CD_3CN	120.1 (13.1)	22.1 (24.4)	13.5	δ(C_3H_5) 75.2 (32.3), 125.4
14	$(CD_3)_2SO$	120.1 (16.0)	16.9 (23.3)	12.5 (4.0)	
15	$(CD_3)_2SO$	120.1 (16.0)	16.4 (29.3)	12.2 (3.3)	

[a] Spectra (67.5 MHz) measured at 20°C with chemical shifts (δ are in ppm (±0.1) to high frequency of $SiMe_4$ and coupling constants (J) are in Hz (±3).
[b] The first numbers given are the chemical shifts and the numbers in parentheses are *J*(CP) coupling constants unless otherwise stated. The signals were normally virtual triplets and the coupling constants listed are $|^nJ(PC) + {}^{n+2}J(PC)|$.
[c] Complex multiplet.
[d] ^3J(PtC).
[e] The figures in parentheses are ^2J(PC) and then ^1J(PtC).
[f] The BPh_4 salt was used for this spectrum.

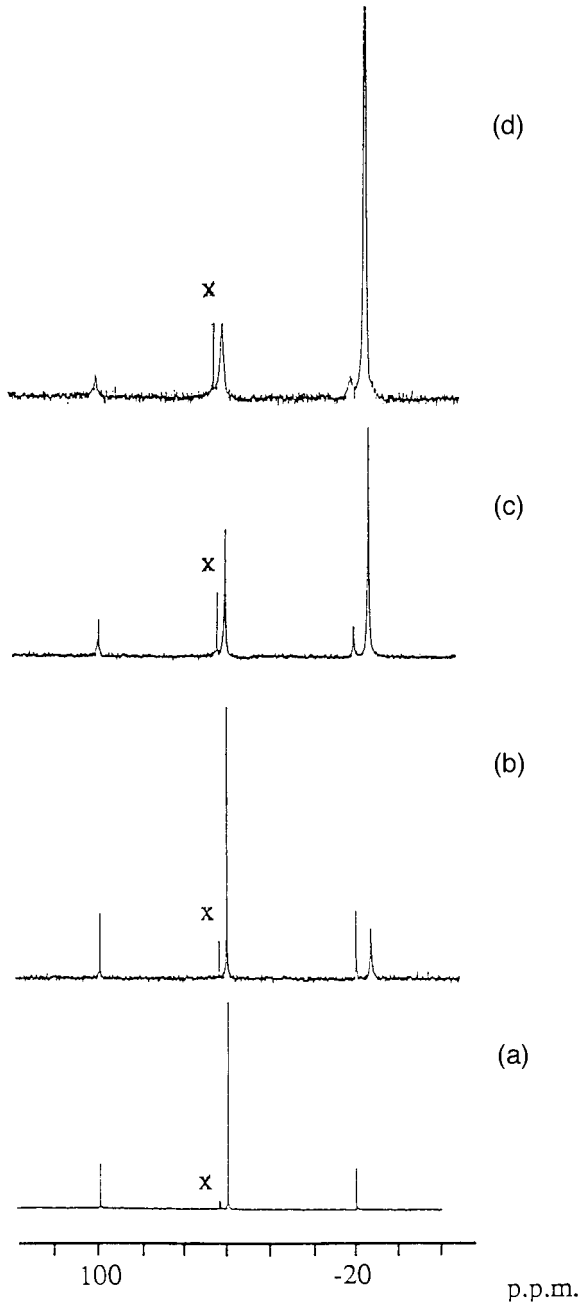


Fig. 1. ^{31}P NMR spectra of [Pt(tcep)$_3$] (**5**) in the presence of (a) no tcep; (b) 1 equiv. tcep; (c) 3 equiv. tcep; (d) 10 equiv. tcep. X = impurity peak (2% intensity of signal for **5**)

previously reported [26] *trans*-[PdCl$_2$(tcep)$_2$] (**7a**) was made from [PdCl$_2$(NCPh)$_2$] and tcep; the corresponding dibromo (**7b**) and diiodo (**7c**) complexes were made by metathesis of **7a** with LiBr and LiI respectively. The *trans* geometry in **7a–c** is confirmed by the appearance of virtual triplets in the ^{13}C NMR spectra (see Tables 1–3 for the characterising data). Treatment of *trans*-[PdCl$_2$(tcep)$_2$] (**7a**) with LiOMe in the presence of 2 equivalents of tcep gave a yellow solid to which we assign the structure [Pd(tcep)$_3$] (**8**) on the basis of elemental analysis, ^{31}P and ^{13}C NMR spectroscopy. The ^{31}P NMR spectrum of the filtrate consisted of a singlet at 42.9 ppm which was assigned to O=P(CH$_2$CH$_2$CN)$_3$. Mason and Verkade [26] previously observed the formation of [Pd(tcep)$_x$] upon treatment of *trans*-[PdCl$_2$(tcep)$_2$] with F$^-$ but the complex was not isolated and x was not defined; since their data concur with ours for **8**, we can conclude that $x = 3$. The ^{31}P NMR spectrum of **8** in the presence of tcep shows broad signals for **8** and free tcep showing that, like its platinum analogue **5**, phosphine exchange is occurring on the NMR timescale but there is no evidence for the formation of a stable [Pd(tcep)$_4$] species.

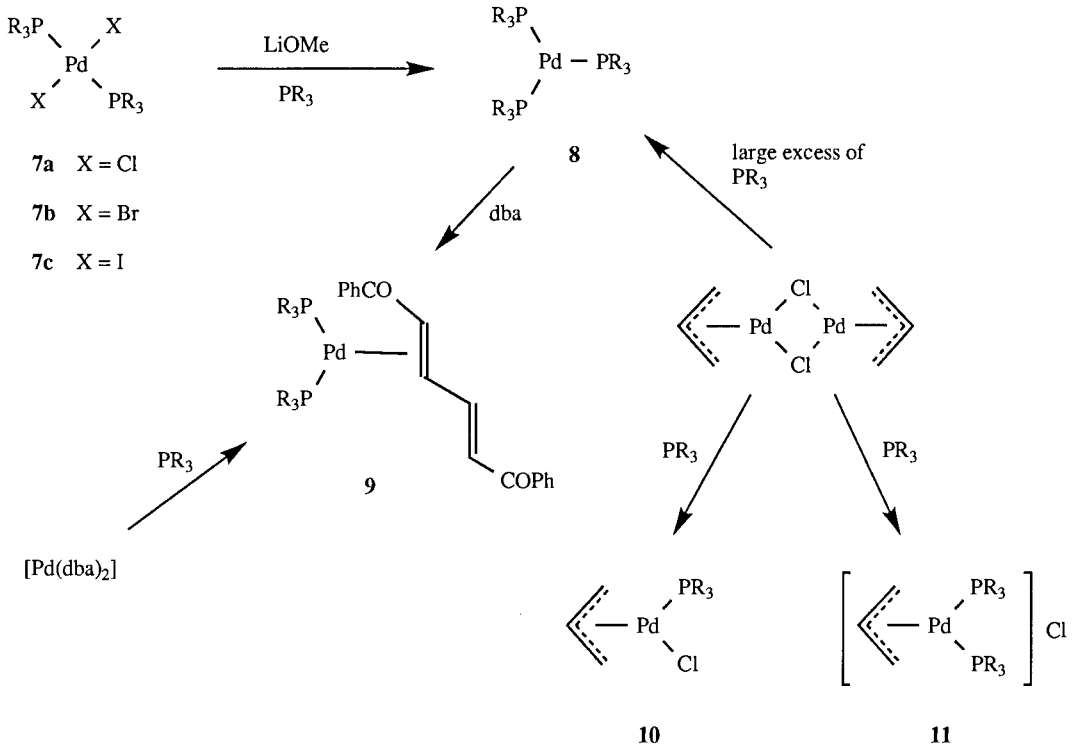
The complex [Pd(tcep)$_2$(η^2-dba)] **9** (dba = dibenzylideneacetone) was formed upon addition of 2 equivalents of tcep to [Pd(dba)$_2$] or one equivalent of dba to complex **8** (see Scheme 2) and has been isolated and fully characterised. When 7 equiv. of tcep is added to solutions of **9**, broadened ^{31}P NMR signals for **9** and tcep are observed indicating tcep exchange on the NMR timescale; however, no signal for **8** was detected showing that, like other bulky PR$_3$ complexes of the type [Pd(PR$_3$)$_2$(η^2-dba)] [38,39] the coordinated dba in **9** is not susceptible to substitution.

The allylpalladium(II) complexes [PdCl(tcep)(η^3-C$_3$H$_5$)] (**10**) and [Pd(tcep)$_2$(η^3-C$_3$H$_5$)]Cl (**11**) were made by treatment of [Pd$_2$(η-Cl)$_2$(η^3-C$_3$H$_5$)$_2$] with 1 or 2 equivalents of tcep (see Scheme 2 and Tables 1–3 for the data). The ionic species **11** is water soluble and the anion can be readily exchanged for BPh$_4$ by treatment of aqueous solutions of **11** with NaBPh$_4$. Addition of an excess of tcep to [Pd$_2$Cl$_2$(η^3-allyl)$_2$] in ethanol gave **8** (a similar reduction occurs with other phosphines [40–42]) but the palladium(0) product was not obtained in pure form using this route.

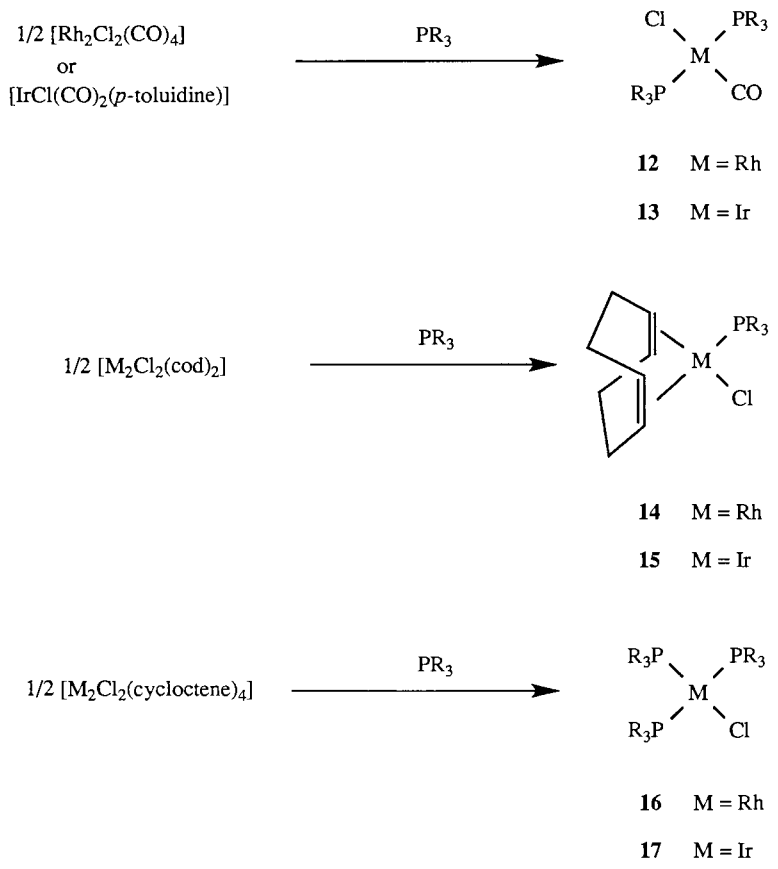
2.3. Rhodium and iridium complexes of tris(cyanoethyl)phosphine

The rhodium and iridium chemistry is summarised in Scheme 3 and characterising data are given in Tables 1–3. The complexes *trans*-[MCl(CO)(tcep)$_2$] M = Rh (**12**) or M = Ir (**13**) are made by treatment of [Rh$_2$Cl$_2$(CO)$_4$] or [IrCl(CO)$_2$(*p*-toluidine)$_2$] with tcep in acetone. The chloro-bridges in [M$_2$(μ-Cl)$_2$(cod)$_2$] are cleaved by addition of 2 equivalents of tcep to give [MCl(cod)(tcep)] M = Rh (**14**) or M = Ir (**15**).

Treatment of [Rh$_2$(μ-Cl)$_2$(cyclooctene)$_4$] with 6 equivalents of tcep in acetone gave [RhCl(tcep)$_3$] (**16**) as unambiguously identified from the doublet of triplets and doublet of doublets observed in the ^{31}P NMR spectra of the reaction solutions. However we were unable to obtain this compound in analytically pure condition because of the presence of small amounts (< 5% by ^{31}P NMR spectroscopy) of unidentified



Scheme 2. Palladium chemistry with tcep (R = CH_2CH_2CN).



Scheme 3. Rhodium and iridium chemistry with tcep (R = CH_2CH_2CN).

rhodium-containing impurities. The iridium analogue $[IrCl(tcep)_3]$ (**17**) was made similarly from $[Ir_2(\mu\text{-}Cl)_2(cyclooctene)_4]$ and tcep in MeCN. The orange solid product was air stable and formed crystals from MeCN solution suitable for X-ray crystallography.

2.4. X-ray crystal structure of $[IrCl(tcep)_3] \cdot 0.5$ Mecn

Fig. 2 shows the molecular structure of complex **17** present in the crystal and Table 4 gives important structural parameters. As expected, the iridium is square planar with small deviations from ideal coordination geometry and the Ir–P distances reflect the low *trans* influence of chloride (Ir–P *trans* to Cl = 2.218(3), *trans* to tcep av. 2.310(3) Å). The P–Ir–P angles are distorted from ideal values as might be expected due to the bulk of the tcep ligands (av. *cis* P–Ir–P 96°, av. *cis* P–Ir–Cl 85°). The deviations from ideal geometry at Ir are most marked in the *trans* angles which are folded (to ca. 164°) so as to reduce the pseudo-symmetry at Ir from D_{4h} (as in an ideal square planar environment) and the crowding in the coordination plane. One of the tcep ligands shows a disorder affecting the conformation of one PCCCN chain [at P(1)], the two images differ in the positions of the α carbons (C(14) and C(14′) and the cyano groups.

As reflected in the torsion angle data given in Table 4 the tcep ligands adopt a variety of conformations about the P–C and C–C(CN) bonds. The variability of tcep conformations in metal complexes has been noted previously. Thus Liu et al. [14] reported that the P–C–C–CN conformations were typically a mix of *gauche* (torsion angles ca. 60° or −60°, g^+ or g^-) or *anti* (torsion angles near ±180°, a). However, it is clear that to describe the conformational behaviour of these ligands (and in turn their cone angles) the M–P–C–C torsion angles must be taken into account as well. Thus in **17** while all the P–C–C–CN conformations (bar one of the disordered chains) are *anti*, in each tcep ligand one Ir–P–C–C chain is *anti*, and the other two are *gauche* (either g^+ or g^-). The cone angles for these tcep ligands were calculated as $\theta/2 = (\theta_1 + \theta_2 + \theta_3)/3$ where θ_i is the angle subtended by the van der Waals envelope of the ith PCCCN chain. The resultant cone angles for the tcep ligands of P(1), P(2) and P(3) are 147 [for either C(14) or C(14′)], 146 and 149° respectively. The effect of the Ir–P–C–C conformations are notable with those which are *anti* leading to lower θ_i of ca. 60° and those which are *gauche* having θ_i ca. 80°. Still larger θ_i are possible if the 'umbrella' conformation is adopted in which all three M–P–C–C are g^- and all three P–C–C–CN are g^+ (as in $[Ag(tcep)_2]^+$ [14]) or in its enantiomeric form (where the signs of all torsion angles are reversed).

In order to explore the generality of these observations, those crystal structures containing tcep coordinated to transition elements were retrieved from the

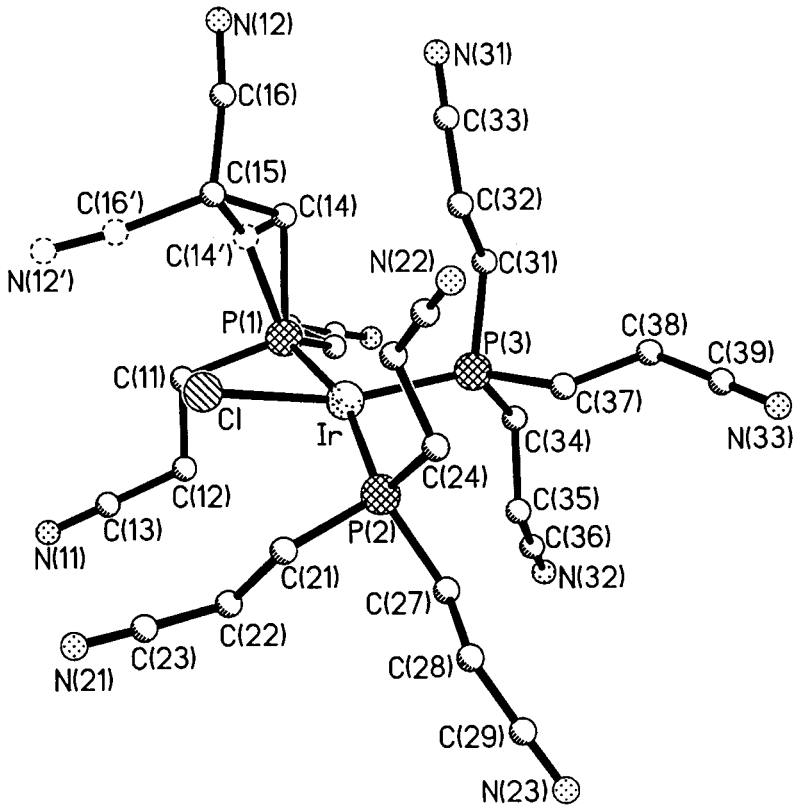


Fig. 2. Molecular structure of (**17**) showing labelling scheme. All hydrogen atoms have been omitted for clarity

Table 4
Selected bond distances (Å) angles (deg) and torsion angles (deg) from the crystal structure of **17**·0.5 MeCN

Ir–P(1)	2.318(3)
Ir–P(2)	2.321(3)
Ir–P(3)	2.218(3)
Ir–Cl	2.386(3)
P(1)–Ir–P(2)	164.8(1)
P(1)–Ir–P(3)	94.9(1)
P(2)–Ir–P(3)	97.5(1)
P(1)–Ir–Cl	83.4(1)
P(2)–Ir–Cl	87.2(1)
P(3)–Ir–Cl	163.6(1)
Ir–P(1)–C(11)–C(12)	−57.9(3)
P(1)–C(11)–C(12)–C(13)	175.9(3)
Ir–P(1)–C(14)–C(15)	−67.3(5)
Ir–P(1)–C(14′)–C(15)	−28.2(5)
P(1)–C(14)–C(15)–C(16)	178.8(5)
P(1)–C(14′)–C(15)–C(16′)	−77.7(6)
Ir–P(1)–C(17)–C(18)	166.0(3)
P(1)–C(17)–C(18)–C(19	177.9(3)
Ir–P(2)–C(21)–C(22)	60.0(3)
P(2)–C(21)–C(22)–C(23)	−166.6(3)
Ir–P(2)–C(24)–C(25)	38.6(3)
P(2)–C(24)–C(25)–C(26)	173.6(3)
Ir–P(2)–C(27)–C(28)	−179.5(3)
P(2)–C(27)–C(28)–C(29)	−178.7(3)
Ir–P(3)–C(31)–C(32)	54.8(3)
P(3)–C(31)–C(32)–C(33)	−164.6(3)
Ir–P(3)–C(34)–C(35)	−59.8(3)
P(3)–C(34)–C(35)–C(36)	166.8(3)
Ir–P(3)–C(37)–C(38)	−170.0(3)
P(3)–C(37)–C(38)–C(39)	−170.3(3)

Cambridge Structural Database (see Section 4). For a conformation space such as that for tcep there are six symmetry equivalent conformations [43,44] as listed below, in which ω_i refer to M–P–C–C torsion angles and τ_i to P–C–C–C torsions in the ith chain M–P–C–C–CN of an M-tcep fragment. As usual the conformation space has a 360° periodicity in all dimensions.

1. $\omega_1, \omega_2, \omega_3; \tau_1, \tau_2, \tau_3$
2. $\omega_2, \omega_3, \omega_1; \tau_2, \tau_3, \tau_1$
3. $\omega_3, \omega_1, \omega_2; \tau_3, \tau_1, \tau_2$
4. $-\omega_1, -\omega_3, -\omega_2; -\tau_1, -\tau_3, -\tau_2$
5. $-\omega_2, -\omega_1, -\omega_3; -\tau_2, -\tau_1, -\tau_3$
6. $-\omega_3, -\omega_2, -\omega_1; -\tau_3, -\tau_2, -\tau_1$

If each torsion angle is assumed to take either *anti* (a), or *gauche* positive (g^+) or *gauche* negative (g^-) then there are seven unique possible conformer types in respect of the sets of three M–P–C–C (ω) conformations as listed below.

A aaa
B $g^+g^+g^+$ ($\equiv g^-g^-g^-$)
C g^+g^+a ($\equiv g^+ag^+; ag^+g^+; g^-g^-a; g^-ag^-; ag^-g^-$)
D g^+aa ($\equiv aag^+; ag^+a; g^-aa; aag^-; ag^-a$)
E g^+g^-a ($\equiv g^-ag^+; ag^+g^-$)
F g^-g^+a ($\equiv g^+ag^-; ag^-g^+$)
G $g^-g^+g^+$ ($\equiv g^+g^-g^+; g^+g^+g^-; g^-g^-g^+; g^-g^+g^-; g^+g^-g^-$)

A similar classification of the sets of three P–C–C–C conformations (torsion angles τ) is also possible. In the case of **17** the Ir–P–C–C (ω) conformer types are **C**, **C** and **F** for P(1), P(2) and P(3), respectively. For each tcep (except the C(14′) image of the P(1) ligand) as noted above all three P–C–C–C conformations are *anti* leading to a fuller description for the tcep ligand conformation as **C**/**A** (for the C(14) image) or **C**/**D** (for the C(14′) image), **C**/**A** and **F**/**A** for the three tcep ligands, where the first letter refers to the set of torsions, ω, about P–C bonds and the second to the set of C–C conformations, τ. Note that the 'umbrella' conformation [14] would be of type **B**/**B** and the fully inverted umbrella **A**/**A** in this notation.

Table 5
M–P–C–C and P–C–C–CN torsion angles in M(tcep) complexes in the CSD

Refcode[a]	ω_1	ω_2	ω_3	τ_1	τ_2	τ_3	Conformer type
ACNICP	−61.6	56.7	178.5	173.2	174.6	78.9	**F**/**D**
BEFDIZ01	−70.3	−47.7	−176.2	178.9	67.1	179.0	**C**/**D**
BEFDIZ01	50.6	68.5	170.1	−60.6	84.4	169.7	**C**/**F**
BEFDIZ02	63.0	−177.9	−58.6	−180.0	70.5	171.1	**C**/**F**
CIZNII	54.8	53.3	54.2	−176.1	175.1	172.6	**B**/**A**
CIZNII	−174.8	51.7	51.9	−177.2	174.6	−173.6	**C**/**A**
CIZNOO	−52.7	−49.9	177.5	−170.1	74.4	171.3	**C**/**D**
CYEPNI	61.7	−169.6	−57.9	−66.2	179.8	−171.9	**F**/**D**
LESNOM	56.6	32.0	−60.1	−66.7	−169.9	−176.9	**G**/**D**
LESNOM01	−62.2	48.3	38.7	61.5	−70.9	−178.9	**G**/**E**
LEXXOB	44.7	60.5	58.5	62.0	177.5	−166.1	**B**/**D**
LEXXOB	176.5	−43.8	−54.3	149.5	176.7	−178.2	**C**/**A**
PERFEX	−42.8	−42.8	−42.8	75.7	75.7	75.7	**B**/**B**
PERFOH	−45.8	64.4	−45.2	179.0	−171.0	−166.4	**G**/**A**
TNITPP	−44.8	−44.8	−44.8	179.4	179.4	179.4	**B**/**D**
TNITPP	58.5	45.7	47.2	−87.1	175.4	167.9	**B**/**A**
ZOZFUP	−39.9	−51.1	58.0	−174.5	75.4	−58.0	**G**/**E**

[a] From Ref. [45,46].

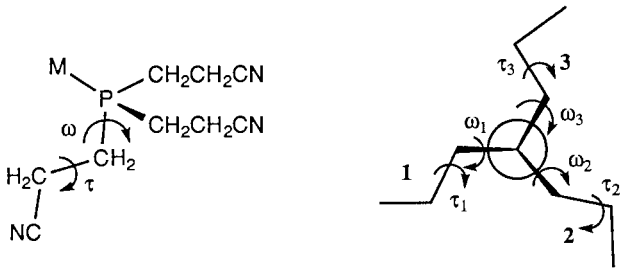


Fig. 3. Labelling scheme for torsion angles describing the M–P–C–C (ω) and P–C–C–CN (τ) conformations.

For the 17 unique tcep ligands located in the CSD (see Section 4, Table 5, Fig. 3) conformer types may be assigned by this procedure. The ω conformer types **B**, **C**, **F** and **G** are observed (5, 6, 2 and 4 examples, respectively), but there are no **A**, **D** or **E** types in the list. In contrast for the P–C–C–CN torsions, τ, there are examples of type **A**, **B**, **D**, **E**, and **F** (5, 1, 7, 2 and 2 examples, respectively) and no examples of types **C** and **D**. While any conclusions drawn from such a small data set must be very tentative, it seems likely that the missing conformer types are likely to be higher in energy than the observed ones, and that the more common ones be of relatively low energy. The absence of any aaa or aag ω conformers (types **A** and **D**) imply that inter-chain interactions must be important. These are precisely the conformations that would lead to small cone angles and there absence is consistent with the ability of tcep to shield low coordination number metals such as the three coordinate Pt(0) and Pd(0) species reported in this paper. The absence of type **E** ω conformers is perhaps not unexpected in view of the high energy of g^+g^- interactions in organic chemistry (as in 1,3 diaxial cyclohexanes). See Ref. [47] for an example of the consequences of such interactions in controlling the conformations of alkyl chains attached to quaternary centres. The additional repulsive effects due to the electrostatic interactions between cyano groups seem likely to enhance these effects.

For any given M–P–C–C–CN chain there are five unique conformation types arising from combinations of ω and τ which are a, g^+ or g^-, as listed below for which the M–P–C–C (ω) conformation is given first as elsewhere.

H a/a
I a/g^+ ($\equiv$ a/g^-)
J g^+/a ($\equiv$ g^-/a)
K g^+/g^+ ($\equiv$ g^-/g^-)
L g^+/g^- ($\equiv$ g^-/g^+)

In **17** only type **H** (3 times), **J** (6 times) and (for one of the disordered chains) **K** chain conformations are observed. As shown in Fig. 4 all of these combinations are observed in the data set of 17 tcep ligands drawn from the CSD. Overall there are 26 chains of type **J** and 11 of type **L**, 6 of type **H**, and 2 each of types **I** and **K**. On the basis of this rather slight evidence there seems to be some local preference for types **J** and **L** although molecular and presumably crystal environment can clearly induce other combinations. Overall in the data set there are 8 *anti* and 39 *gauche* conformations at the P–C bonds, and 32 *anti* and 15 *gauche* conformations at the C–C(CN) bonds. While these individual bond conformation frequencies may say something about their energetic preferences, it is clear that it is important to

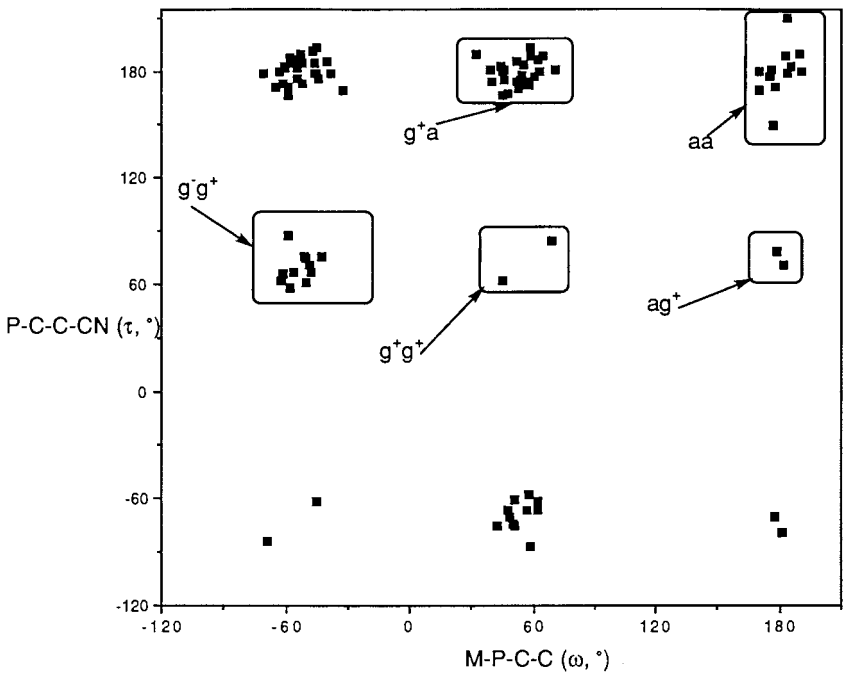


Fig. 4. Plot of τ vs. ω for all M–PCCCN fragments located in the CSD after symmetry expansion and application of 360° periodicity.

consider the way that torsion angles are combined when analysing the conformational preferences of this type of ligand. A complete analysis of the combinations of ω and τ triples has not been carried out here because of the paucity of data. A more detailed study of these preferences for more plentiful ligands such as PEt_3 or $P(OR)_3$ would seem warranted. We note that similar conformational behaviour is seen in other recently reported structures of tcep complexes not yet in the CSD: [AuBr(tcep)] (**G / E**) [48]; $[Au(tcep)_2 \cdot Au(CN)_2]$ (**B / A** and **C / A**) [49]; $[Mo_2Cl_4(tcep)_2(NCR)_2]$ (R = Me, **B / A** and **B / A**), R = Et (**C / A** and **C / A**), R = Pr^i (**C / A** and **C / A**) [50].

3. Conclusion

From the chemistry described here, two striking features of the coordination chemistry of tcep have emerged: (i) tcep can stabilise low valent metals which is manifest in the high air-stability of the complexes with platinum(0), palladium(0) and iridium(I); (ii) tcep can stabilise coordinative unsaturation as observed in the 3-coordinate palladium(0) and platinum(0) complexes. These properties are more reminiscent of a phosphite or a bulky phosphine ligand than of a small trialkyl phosphine. Thus our results provide further experimental support for the idea that the β-cyano substituents (i) may engender significant π-acceptor capacity on tcep and (ii) make the cone angle of tcep much greater than would be predicted from a simple model because of repulsive CN · · · CN electrostatic forces.

4. Experimental

All reactions were carried out under a nitrogen atmosphere unless otherwise stated and solvents dried, when necessary, by refluxing over the appropriate drying reagents (calcium hydride for dichloromethane, sodium/benzophenone for diethyl ether, toluene and *n*-hexane) and distilled under nitrogen prior to use. Commercial reagents were used as supplied unless otherwise stated; the phosphonium salt $[P(CH_2OH)_4]Cl$ was obtained from Albright and Wilson as an 80% solution in water and from this, $P(CH_2CH_2CN)_3$ (tcep) made by the literature method [28–30] or obtained from Strem Chemicals. The following starting materials were prepared according to literature methods: $[PtCl_2(cod)]$ [51], $[PtMe_2(cod)]$ [52], $[PtCl(CH_3)(cod)]$ [53], $[Pt(norbornene)_3]$ [54], $[PdCl_2(NCPh)_2]$ [55], $[Pd(dba)_2]$ [56], $[Rh_2Cl_2(CO)_4]$ [57], [IrCl(CO)$_2$(*p*-toluidine)] [58], $[Rh_2Cl_2(cod)_2]$ [59], $[Ir_2Cl_2(cod)_2]$ [60], $[Rh_2Cl_2(cyclooctene)_4]$ [61], $[Ir_2Cl_2(cyclooctene)_4]$ [60].

4.1. Preparation of trans-$[PtCl_2(tcep)_2]$ (1)

A solution of tcep (413 mg, 2.14 mmol) in CH_2Cl_2 (6 cm^3) was added dropwise over 3 min to a solution of $[PtCl_2(cod)]$ (400 mg, 1.07 mmol) in CH_2Cl_2 (20 cm^3) to give an off-white solid which was filtered off, washed with CH_2Cl_2 (1 cm^3) and then dried in vacuo. The product (650 mg, 93%) was identified as **1** by comparison of its NMR spectra with the literature [16,17].

4.2. Preparation of cis-$[PtMe_2(tcep)_2]$ (2)

A solution of tcep (326 mg, 1.87 mmol) in acetone (5 cm^3) was added to a solution of $[PtMe_2(cod)]$ (312 mg, 0.936 mmol) in acetone (20 cm^3) and the resulting colourless solution was stirred for 10 min. The solution was then concentrated to 1–2 cm^3 and the white product was precipitated by addition of diethyl ether (30 cm^3) and then filtered off, washed with diethyl ether (5 cm^3) and dried in vacuo (554 mg, 97%). ^{1}H NMR (270 MHz, $(CD_3)_2CO$): 2.88 and 2.50 (complex multiplets, coordinated tcep resonances) 0.43 (br. s, ^2J(PtH) 62.1 Hz, Pt-CH_3). Other characterising data are given in Tables 1–3.

4.3. Preparation of trans-$[PtMeCl(tcep)_2]$ (3)

A solution of tcep (163 mg, 0.844 mmol) in acetone (5 cm^3) was added to a solution of [PtMeCl(cod)] (149 mg, 0.421 mmol) in acetone (10 cm^3) and the resulting colourless solution was stirred for 10 min. The solution was then concentrated to 1–2 cm^3 and the white product was precipitated by addition of diethyl ether (30 cm^3) and then filtered off, washed with diethyl ether (5 cm^3) and dried in vacuo (240 mg, 90%). ^{1}H NMR (270 MHz, $(CD_3)_2CO$): 2.98 and 2.58 (complex multiplets, coordinated tcep resonances); 0.50 (d, ^3J(PH) 6.4 Hz, ^2J(PtH) 80.1 Hz, Pt-CH_3). Other characterising data are given in Tables 1–3.

4.4. Preparation of $[PtHCl(tcep)_2]$ (4)

Sodium borohydride (30 mg, 0.793 mmol) was added in small portions over 10 min to a solution of *trans*-$[PtCl_2(tcep)_2]$ (500 mg, 0.828 mmol) in acetonitrile (30 cm^3). The solution was stirred for 1 h and then the solvent was evaporated to dryness under reduced pressure. Water (30 cm^3) was added to the residue and the white solid was filtered off in air, washed with methanol (20 cm^3), diethyl ether (30 cm^3) and then dried in vacuo to give the product (360 mg, 71%). ^{1}H NMR (270 MHz, CD_3CN): 2.76 and 2.36 (complex multiplets, coordinated tcep resonances); −17.05 (t, ^2J(PH) 14.8 Hz, ^1J(PtH) 1244 Hz, Pt–*H*). IR (nujol mull, CsI plates, cm^{-1}): 2245 (m, ν(CN)), 2203(m, ν(PtH)), 285

(m, ν(PtCl)). Other characterising data are given in Tables 1–3.

4.5. Preparation of [Pt(tcep)$_3$] (5)

(a) A solution of tcep (1.220 g, 6.31 mmol) in acetone (20 cm^3) was added dropwise over 1 min to a solution of [Pt(norbornene)$_3$] (1.008 g, 2.11 mmol) in toluene (80 cm^3) to give a yellow precipitate immediately. After stirring the mixture for 3 h, the yellow solid was filtered off under nitrogen. The product **5** was purified by dissolving it in acetone (60 cm^3) and then adding toluene (100 cm^3) to reprecipitate it (1.405 g, 86%). IR (nujol mull) showed ν(CN) at 2250 cm^{-1}. Other characterising data are given in Tables 1–3.

(b) Sodium borohydride (30 mg, 0.793 mmol) was added to a suspension of [PtCl$_2$(tcep)$_2$] (174 mg, 0.266 mmol) and tcep (54 mg, 0.280 mmol) in ethanol (14 cm^3) and the mixture was heated to 60°C and stirred for 70 min and then allowed to cool to room temperature. The yellow precipitate was filtered off, redissolved in acetone (10 cm^3) and reprecipitated by addition of diethyl ether (20 cm^3) to give pure **5** (206 mg, 65%).

(c) Complex **5** was the only phosphorus-containing product observed by ^{31}P NMR spectroscopy when a solution of **4** (24 mg, 0.039 mmol) and tcep (8 mg, 0.041 mmol) in (CD$_3$)$_2$SO (0.4 cm^3) was treated with triethylamine (0.020 cm^3).

4.6. Preparation of [PtH(tcep)$_3$]BF$_4$ (6)

85% HBF$_4$ in diethyl ether (0.040 cm^3, 0.238 mmol) was added to a solution of [Pt(tcep)$_3$] (125 mg, 0.161 mmol) in acetone (6 cm^3) and the resulting colourless solution was stirred for 10 min. The solution was then concentrated to 1–2 cm^3 and the white product was precipitated by addition of diethyl ether (20 cm^3) and then filtered off, washed with diethyl ether (2 cm^3) and dried in vacuo (108 mg, 77%). ^{1}H NMR (270 MHz, (CD$_3$)$_2$SO): 2.78 and 2.51 (complex multiplets, coordinated tcep resonances); −7.06 (t, ^2J(PH) 157.5, and 15.7 Hz, ^1J(PtH) 760 Hz, Pt–*H*). Other characterising data are given in Tables 1–3.

4.7. Preparation of trans-[PdCl$_2$(tcep)$_2$] (7a)

A solution of tcep (534 mg, 2.76 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added dropwise over 3 min to a solution of [PdCl$_2$(NCPh)$_2$] (530 mg, 1.38 mmol) in CH$_2$Cl$_2$ (10 cm^3)and the mixture stirred for a further 10 min. The yellow solid product was filtered off, washed with CH$_2$Cl$_2$ (1 cm^3) and then dried in vacuo (762 mg, 98%). The corresponding bromo (**7b**) and iodo (**7c**) complexes were made in 82 and 96% yields by treatment of **7a** in CH$_2$Cl$_2$ with acetone solutions of LiBr and LiI respectively. See Tables 1–3 for characterising data.

4.8. Preparation of [Pd(tcep)$_3$] (8)

A solution of lithium methoxide in methanol (0.1 M, 32.0 cm^3, 3.19 mmol) was added to dry ethanol (30 cm^3) and then *trans*-[PdCl$_2$(tcep)$_2$] (450 mg, 0.798 mmol) and tcep (324 mg, 1.68 mmol) were added. The solution was refluxed for 2 h to afford a yellow precipitate which, when cool, was filtered off, washed with diethyl ether (20 cm^3) and dried in vacuo (506 mg, 92%). See Tables 1–3 for characterising data.

4.9. Preparation of trans-[Pd(η^2-dba)(tcep)$_2$] (9)

A solution of tcep (283 mg, 1.466 mmol) in acetone (6 cm^3) was added to a solution of [Pd(η^2dba)$_2$] (40 mg, 0.100 mmol) in toluene (40 cm^3) and immediately a yellow precipitate formed with an orange solution. The mixture was stirred for 2 h and then the yellow solid was filtered off, washed with toluene (2 cm^3) and dried in vacuo (355 mg, 70%). See Tables 1–3 for characterising data.

4.10. Preparation of trans-[PdCl(η^3-C$_3$H$_3$)(tcep)] (10)

A solution of tcep (196 mg, 1.01 mmol) in acetone (5 cm^3) was added to a solution of [Pd$_2$Cl$_2$(η^3-C$_3$H$_3$)$_2$](185 mg, 0.506 mmol) in acetone (10 cm^3) and the resulting pale yellow solution was stirred for 10 min. The solution was then concentrated to 1 cm^3 and the yellow product was precipitated by addition of diethyl ether (20 cm^3) and then filtered off, washed with diethyl ether (5 cm^3) and dried in vacuo (353 mg, 93%). IR (nujol mull, CsI plates, cm^{-1}): 2250 (m, ν(CN)), 290 (m, ν(PdCl)). Other characterising data are given in Tables 1–3.

4.11. Preparation of trans-[Pd(η^3-C$_3$H$_3$)(tcep)$_2$]Cl (11)

A solution of tcep (345 mg, 1.792 mmol) in acetone (10 cm^3) was added to a solution of [Pd$_2$Cl$_2$(η^3-C$_3$H$_3$)$_2$] (162 mg, 0.448 mmol) in acetone (10 cm^3) and the resulting mixture was stirred for 10 min. The white solid product was filtered off, washed with acetone (1 cm^3) and dried in vacuo (279 mg, 55%). See Tables 1–3 for characterising data.

4.12. Preparation of trans-[RhCl(CO)(tcep)$_2$] (12)

A solution of tcep (78 mg, 0.400 mmol) in acetone (2 cm^3) was added to a solution of [Rh$_2$Cl$_2$(CO)$_4$] (40 mg, 0.100 mmol) in acetone (10 cm^3) and the resulting solution was stirred for 40 min. The solvent was then

evaporated to dryness to give the yellow solid product (91 mg, 82%). See Tables 1–3 for characterising data.

4.13. Preparation of trans-[IrCl(CO)(tcep)$_2$] (**13**)

A solution of tcep (55 mg, 0.240 mmol) in acetone (2 cm^3) was added to a solution of [IrCl(CO)$_2$(*p*-toluidine)] (48 mg, 0.120 mmol) in acetone (10 cm^3) and the resulting solution was stirred for 2 h. The solution was then concentrated to ca. 1 cm^3 and then pentane (30 cm^3) added to give the yellow solid product (58 mg, 75%). IR (nujol mull, CsI plates, cm^{-1}): 2245 (m, ν(CN)), 1955 (s, ν(CO)). Other characterising data are given in Tables 1–3.

4.14. Preparation of [RhCl(tcep)(cod)] (**14**)

A solution of tcep (138 mg, 0.714 mmol) in acetone (4 cm^3) was added to a solution of [Rh$_2$Cl$_2$(cod)$_2$] (175 mg, 0.355 mmol) in acetone (10 cm^3) and the resulting solution was stirred for 15 min. The solution was then concentrated to ca. 1 cm^3 and then diethyl ether (25 cm^3) added to give the yellow solid product (292 mg, 93%). The iridium analogue **15** was made similarly from [IrCl(tcep)(cod)] in 82% yield. See Tables 1–3 for characterising data.

4.15. Preparation of [IrCl(tcep)$_3$] (**17**)

Solid [Ir$_2$Cl$_2$(cyclooctene)$_4$] (119 mg, 0.133 mmol) was added to a solution of tcep (157 mg, 0.813 mmol) in acetonitrile (20 cm^3) and the resulting solution was stirred for 30 min. The solution was then slowly concentrated under reduced pressure until orange crystals separated from the solution. The product (220 mg, 59%) was then filtered off. The rhodium analogue **16** was made similarly [Rh$_2$Cl$_2$(cyclooctene)$_4$] in acetone in 65% yield but was not obtained free from an impurity assigned to the O$_2$ adduct [RhCl(O$_2$)(tcep)$_3$].

4.16. Structure determination of [IrCl(tcep)$_3$] · 0.5MeCN (**17**) · 0.5 MeCN

Crystals suitable for X-ray crystallography were obtained by slow evaporation of MeCN solutions of **17** under reduced pressure. *Crystal data*: $C_{28}H_{37.5}ClIrN_{9.5}P_3$, $M = 827.74$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.373(4)$ Å, $b = 12.301(5)$ Å, $c = 16.645(6)$ Å, $\alpha = 74.26(3)°$, $\beta = 85.41(3)°$, $\gamma = 69.07(3)°$, $V = 1725.49(1.31)$ Å^3, $Z = 2$, $D_c = 1.35$ g cm^{-3}, $\mu = 4.1$ mm^{-1}, $F(000) = 854$, $T = 295$ K, crystal size $0.24 \times 0.24 \times 0.12$ mm, index ranges $-12 \le h \le 12$, $-15 \le k \le 15$, $-20 \le l \le 20$; transmission coefficient range 0.47–0.96. X-ray diffraction measurements on a single crystal mounted in a thin-walled glass capillary were made with graphite monochromated Mo–K$_\alpha$ X-rays ($\bar{\lambda} = 0.71073$ Å) using a Siemens four-circle R3m/V diffractometer. Cell dimensions were determined from setting angles of 25 reflections. A total of 6508 intensity data were collected for a hemisphere of reciprocal space $2\theta < 50.0°$ by $\theta/2\theta$ scans and corrected for Lorentz, polarisation, long-term intensity decay of 8.9%, and for absorption effects on the basis of azimuthal scan data. Of the data, 6106 were unique (R_{int} 0.023). The structure was solved by Patterson methods, and refined by full-matrix least-squares against F against all 4675 data with $I > 1.5\sigma(I)$ with weights, w, set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $g = 0.0008$. All non-hydrogen atoms heavier than carbon were refined without positional constraints and assigned anisotropic displacement parameters (except for the solvent nitrogen). All carbon atoms were refined without positional constraints and atoms C16, C16′, C19, C23, C26, C29, C33, C36, C39, were assigned anisotropic displacement parameters. Disorder was modelled in one tcep ligand (P(1)) with a two-site model used to describe the positions of C14, C16, N12 [occupancy 0.48(1)] and C14′, C16′ and N12′ [occupancy 0.52(1)]. The acetonitrile of crystallisation is disordered about a centre of inversion with atoms having occupancy 0.5. All hydrogen atoms were assigned fixed isotropic displacement parameters and were constrained to ideal geometries. Final difference syntheses showed no chemically significant features, the largest being close to the metal atom. Refinements converged to residuals $R = 0.0556$, $R_w = 0.0572$, $S = 1.17$. [3] Complete atomic coordinates, displacement parameters, bond distances and angles have been deposited. All calculations were made with programs of the SHELXTL-PLUS system [62]. Complex neutral-atom scattering factors were taken from Ref. [63].

4.17. Data retrieval

Crystal structures containing the fragment [M(tcep)] (M = transition metal) were located from the Cambridge Structural Database (CSD) using the QUEST program [45,46]. Data for these crystal structures were retrieved from the October 1996 version of CSD. The data files retrieved were screened and only structures which fulfilled all of the following criteria were retained for further analysis.

1. R factor ≤ 0.11
2. Atomic coordinates included in CSD.
3. No disorder within the fragment
4. ‘perfect match’ between crystallographic and chemical connectivity, and no errors by CSD definitions.

The final data files contained 17 fragments from 11

[3] $R = \Sigma|\Delta|/\Sigma|F_o|$; $wR = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$; $S = [\Sigma w\Delta^2/(\text{N.O.}-\text{N.V.})]^{1/2}$; $\Delta = F_o - F_c$.

structures. The values of the torsion angles (τ_i, $i = 1,3$; ω_i, $i = 1,3$) were calculated for each fragment with PCCCN chains numbered 1–3 anti-clockwise as viewed in Fig. 4.

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