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Syntheses and structures of monoplatinum model complexes for diplatinum polyynediyl adducts $L_nPt(C{\equiv}C)_zPtL_n$

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Abstract

The CuI-catalyzed reactions of *trans*-$(Ph_3P)_2PtCl_2$ with $HC{\equiv}CSiMe_3$ or $HC{\equiv}CC{\equiv}CSiMe_3$ (greater than two equivalents, $HNEt_2$), and *trans*-(*p*-tol)$(Ph_3P)_2PtCl$ (**4**) or *trans*-$(C_6F_5)(p\text{-tol}_3P)_2PtCl$ with $HC{\equiv}CC{\equiv}CH$, give *trans*-$(Ph_3P)_2Pt(C{\equiv}CSiMe_3)_2$ (**2**), *trans*-$(Ph_3P)_2Pt(C{\equiv}CC{\equiv}CSiMe_3)_2$ (**3**), *trans*-(*p*-tol)$(Ph_3P)_2PtC{\equiv}CC{\equiv}CH$ (**5**), and *trans*-$(C_6F_5)(p\text{-tol}_3P)_2PtC{\equiv}CC{\equiv}CH$ (**7**) in 74–81% yields. These compounds are characterized crystallographically, and their physical properties compared. A convenient three-step synthesis of **4** from $(COD)PtCl_2$ is described.

Keywords: Platinum; Alkynyl and butadiynyl complexes; Hagihara coupling; Crystal structures

1. Introduction

This special issue of *J. Organomet. Chem.* celebrates a Symposium hosted by the Chemistry Department of the University of Heidelberg on the subject 'Interactions of π Systems with Metals'. This rich theme has received particular attention in Heidelberg for some time, and many of the pioneering contributions of these accomplished scientists to one of whom this paper is dedicated are detailed elsewhere in this volume. We have had a sustained interest in this topic, involving subjects such as chiral recognition in π complexes of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ [1], or more recently complexes in which sp carbon chains span two transition metals, $L_nMC_xM'L'_{n'}$ [2]. This contribution deals with complexes relevant to the second subject, which has also been of great interest in other laboratories [3].

Compounds of the formula $L_nMC_xM'L'_{n'}$ can exist in a variety of valence forms (e.g. M–C, M=C, or M≡C systems) and electronic ground states. They exhibit numerous fascinating physical and chemical properties. In many cases, interactions between the metals or endgroups — which may be like or unlike — play key roles. In order to analyze endgroup–endgroup interactions accurately, properties of monometallic model complexes $L_nMC_xR_m$ must be precisely defined. Two recent papers provide good illustrations. The first, a collaboration of our group and Lapinte's [4], details a variety of manifestations of iron–rhenium interactions as a function of the oxidation state in heterobimetallic C_4 complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C_4)(\eta^2\text{-dppe})Fe(\eta^5\text{-}C_5Me_5)]^{n+}\,nPF_6^-$ $(n = 0\text{–}2)$. Analyses required many measurements on monoiron and monorhenium model compounds, and the analogous diiron and dirhenium C_4 complexes. The second is a theoretical analysis of *odd* carbon-chain complexes $[(\eta^5\text{-}C_5R_5)(NO)(PR'_3)ReC_xML_n]^{n+}$ $(x = 3, 5, 7, 9)$, some of which have been prepared and the others that remain to be synthesized [5]. Structural, electronic, and thermodynamic data revealed strong metal–metal interactions in some cases $(ML_n = Mn/Re(CO)_2(\eta^5\text{-}C_5H_5))$, but not the others $(ML_n = W(OMe)_3)$.

We have recently communicated a new series of PtC_xPt complexes $(x = 8, 12, 16)$ with polyynediyl chains and (*p*-tol)$(Ph_3P)_2Pt$, (*p*-tol)$(p\text{-tol}_3P)_2Pt$, or

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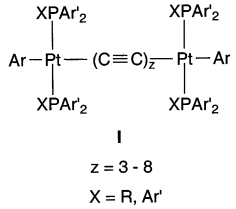
$(C_6F_5)(p\text{-}tol_3P)_2Pt$ endgroups (see **I**) [6–8]. This series of compounds, which features π and σ interactions between platinum and $(C{\equiv}C)_z$ or $(C{\equiv}C)_zPt$ segments, is rapidly being extended, as detailed in our oral contribution to this symposium. Thus, there is a distinct need for the synthesis and physical characterization of monoplatinum model complexes. In this paper, we report the syntheses, spectroscopic characterization, and crystal structures of four such species, two of which apply to the above PtC_xPt systems and two of which anticipate our future efforts in this area.



I

z = 3 - 8

X = R, Ar'

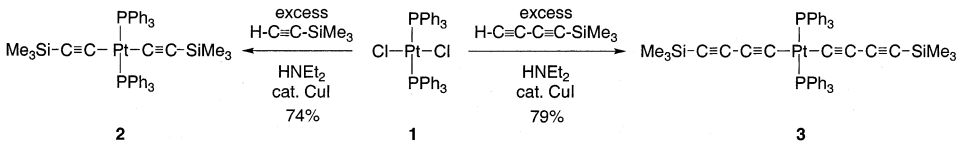
(1)

2. Results

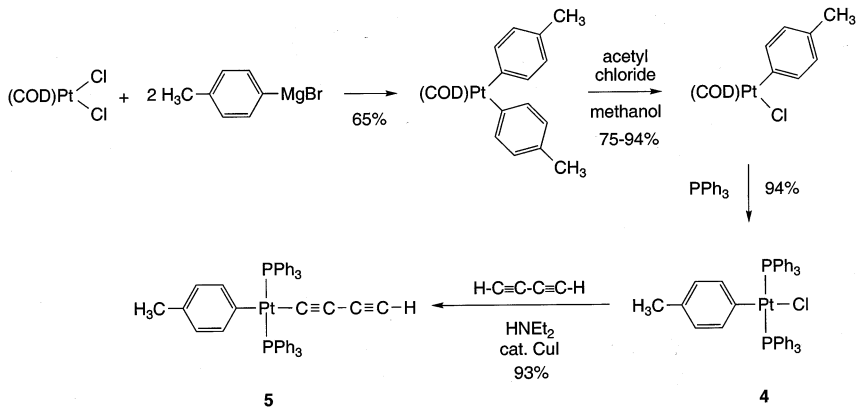
As shown in Scheme 1, the commercially available dichloride complex *trans*-$(Ph_3P)_2PtCl_2$ (**1**) was suspended in the amine solvent $HNEt_2$. An excess of commercial $HC{\equiv}CSiMe_3$ and a catalytic amount of CuI were added. The mixture was stirred at 60 °C, and workup gave the bis(alkynyl) complex *trans*-$(Ph_3P)_2Pt(C{\equiv}CSiMe_3)_2$ (**2**) in 74% yield. Similar conditions have been used to prepare many other platinum alkynyl species [9]. Complex **2**, and all new compounds below, were characterized by microanalysis, and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopies (Section 4). The *trans* stereochemistry followed from the NMR data, which featured diagnostic $^1J(^{31}P,^{195}Pt)$ values [10] and virtual coupling patterns of the phenyl ^{13}C signals [11].

A similar reaction of **1** and easily prepared $HC{\equiv}CC{\equiv}CSiMe_3$ [12] gave the analogous bis(1,3-diynyl) complex *trans*-$(Ph_3P)_2Pt(C{\equiv}CC{\equiv}CSiMe_3)_2$ (**3**) in 79% yield (Scheme 1). Interestingly, **3** was first obtained as a by-product in the analogous reaction of the monochloride complex *trans*-$(p\text{-tol})(Ph_3P)_2PtCl$ (**4**) and $HC{\equiv}CC{\equiv}CSiMe_3$ ($HNEt_2$, cat. CuI). In a formal sense, this requires a protolytic cleavage of the *p*-tolyl ligand by the acidic HCl or $[H_2NEt_2]^+Cl^-$ by-product, followed by the platinum–carbon bond formation.

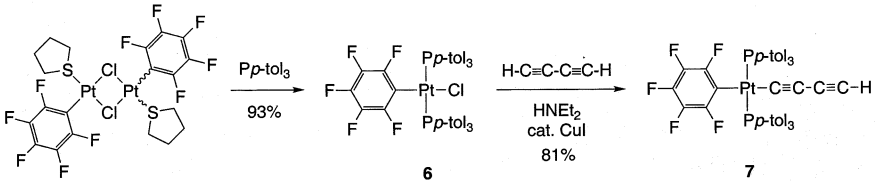
The complex *trans*-$(p\text{-tol})(Ph_3P)_2PtCl$ (**4**) has been previously synthesized [13], but by the thermal isomerization of the *cis* isomer. We therefore describe a more direct sequence, shown in Scheme 2. First, the reaction of $(COD)PtCl_2$ [14] and commercial *p*-tolMgBr (2.5 equivalents) gave $(COD)Pt(p\text{-tol})_2$ (65%), a conversion previously effected with the tin reagent *p*-$tolSnMe_3$ [15]. In an approach used earlier for alkyl chloride complexes (R)(COD)PtCl [14], acetyl chloride (1.0–1.7 equivalents) and methanol were added, generating HCl. Workup gave $(p\text{-tol})(COD)PtCl$ (75–94%), a compound previously obtained from $(COD)PtCl_2$ and one equivalent of *p*-$tolSnMe_3$ [15]. Subsequent reaction with PPh_3 afforded **4** in 94% yield (Scheme 2). A $HNEt_2$ solution of **4** and CuI (7 mol%) was treated with an excess of easily generated $HC{\equiv}CC{\equiv}CH$ [16] in THF. Workup gave the target 1,3-butadiynyl complex *trans*-$(p\text{-tol})(Ph_3P)_2PtC{\equiv}CC{\equiv}CH$ (**5**) in 93% yield.



Scheme 1. Syntheses of $Pt(C{\equiv}C)_zSiMe_3$ complexes.



Scheme 2. Synthesis of a *p*-tolyl 1,3-butadiynyl complex.



Scheme 3. Synthesis of a pentafluorophenyl 1,3-butadiynyl complex.

Table 1
Summary of crystallographic data

Complex	**2**	**3**·ethanol	**5**	**7**
Empirical formula	$C_{46}H_{48}P_2PtSi_2$	$C_{52}H_{54}OP_2PtSi_2$	$C_{47}H_{38}P_2Pt$	$C_{52}H_{43}F_5P_2Pt$
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius CAD4	Nonius KappaCCD
Temperature (K)	200(0.1)	200(0.1)	291(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$I2/a$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (Å)	7.7736(4)	14.4899(9)	10.507(7)	13.0595(3)
b (Å)	12.0982(4)	14.2589(6)	10.6886(15)	14.6995(3)
c (Å)	12.1277(5)	23.7535(14)	18.149(6)	14.7397(3)
α (°)	79.091(2)	90	102.278(18)	114.500(1)
β (°)	75.2346(14)	102.651(2)	83.75(4)	99.310(1)
γ (°)	74.468(2)	90	105.66(2)	110.010(1)
V (Å^3)	1053.50(8)	4788.6(5)	1914.8(14)	2261.61(8)
Z	1	4	2	2
D_{calc} (g cm^{-3})	1.441	1.398	1.491	1.498
Absorption coefficient (mm^{-1})	3.493	3.083	3.779	3.228
Crystal size (mm^3)	$0.28 \times 0.25 \times 0.15$	$0.23 \times 0.18 \times 0.12$		$0.40 \times 0.30 \times 0.30$
Theta range for data collection (°)	3.60–22.66	1.68–24.75	2.02–24.97	4.10–27.52
Index ranges	$0 \le h \le 8$, $-12 \le k \le 12$, $-12 \le l \le 13$	$0 \le h \le 17$, $-16 \le k \le 16$, $-27 \le l \le 27$	$0 \le h \le 12$, $-12 \le k \le 12$, $-21 \le l \le 21$	$-15 \le h \le 16$, $-19 \le k \le 17$, $-19 \le l \le 19$
Reflections collected	2689	5482	7149	15 748
Independent reflections	2689	3460	6744	10 287
Reflections [$I > 2\sigma(I)$]	2689	2923	6119	9548
Data/restraints/parameters	2689/–/233	3460/–/268	6119/–/451	10 287/1/541
Goodness-of-fit on F^2	1.060	1.105	1.099	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0194$; $wR_2 = 0.0498$	$R_1 = 0.0371$; $wR_2 = 0.0853$	$R_1 = 0.0267$; $wR_2 = 0.0696$	$R_1 = 0.0299$; $wR_2 = 0.0780$
R indices (all data)	$R_2 = 0.0194$; $wR_2 = 0.0498$	$R_1 = 0.0473$; $wR_2 = 0.0927$	$R_1 = 0.321$; $wR_2 = 0.0720$	$R_1 = 0.0337$; $wR_2 = 0.0810$
Largest difference peak and hole (e Å^{3-})	1.077 and −0.697	1.522 and −1.046	0.862 and −0.680	1.671 and −2.460

The pentafluorophenyl tetrahydrothiophene (SR_2) complex $[(C_6F_5)Pt(SR_2)(\mu\text{-}Cl)]_2$ [17] has been shown earlier to react with phosphines to give species of the formula *trans*-$(C_6F_5)(L)_2PtCl$ [10a,18]. As shown in Scheme 3, reaction with *p*-tol_3P gave the bis(phosphine) complex *trans*-$(C_6F_5)(p\text{-}tol_3P)_2PtCl$ (**6**) in 93% yield after workup. Reaction with $HNEt_2$, CuI, and HC≡CC≡CH as with **4** gave the target 1,3-butadiynyl complex *trans*-$(C_6F_5)(p\text{-}tol_3P)_2PtC{\equiv}CC{\equiv}CH$ (**7**) in 81% yield.

Complexes **2**, **3**, **5**, and **7** were white to pale yellow air-stable powders. Crystals were grown as described in Section 4. The X-ray structures were determined, and general data are summarized in Table 1. The corresponding ORTEP diagrams, which confirm the structural assignments, are given in Figs. 1–4. The key bond lengths and bond angles are given in Table 2. The ^{13}C-NMR spectra of **3**, **5**, and **7** showed C≡CC≡C signals with chemical shift patterns analogous to those of the other 1,3-butadiynyl and 1,3-silylbutadiynyl platinum and rhenium complexes [2e,6,7]. The UV–vis spectrum of the bis(1,3-butadiynyl) complex **3** exhibited bands at 319 and 339 nm (ε 12 000 and 26 400 M^{-1} cm^{-1}, CH_2Cl_2). In contrast, the mono(1,3-bu-

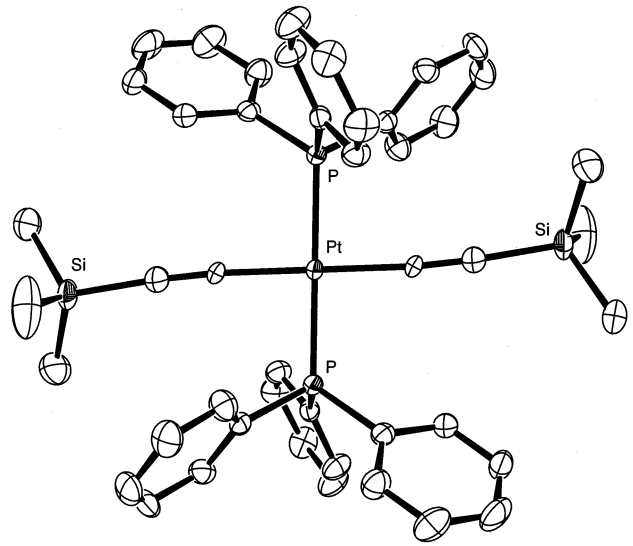


Fig. 1. Molecular structure of *trans*-$(Ph_3P)_2Pt(C{\equiv}CSiMe_3)_2$ (**2**).

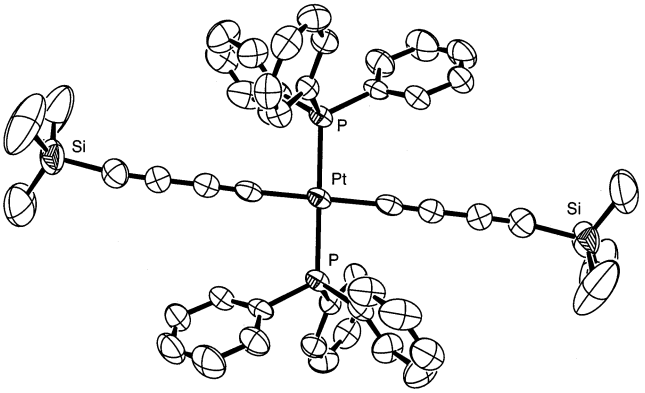


Fig. 2. Structure of *trans*-$(Ph_3P)_2Pt(C{\equiv}CC{\equiv}CSiMe_3)_2$·ethanol (**3**·ethanol) with the solvate omitted.

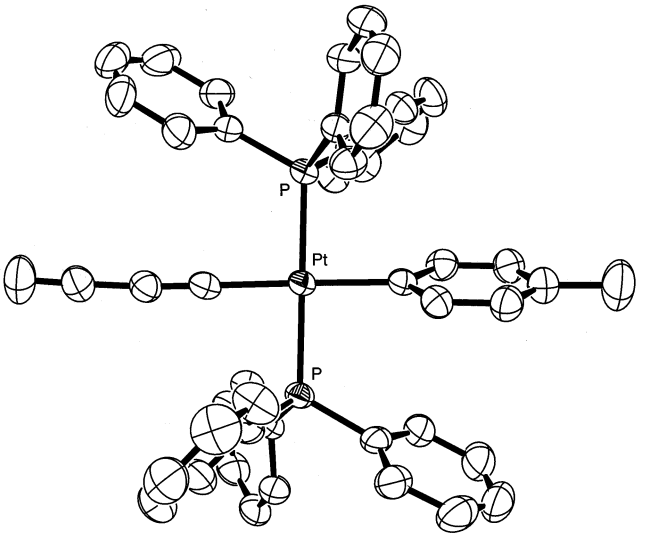


Fig. 3. Molecular structure of *trans*-(*p*-tol)$(Ph_3P)_2PtC{\equiv}CC{\equiv}CH$ (**5**).

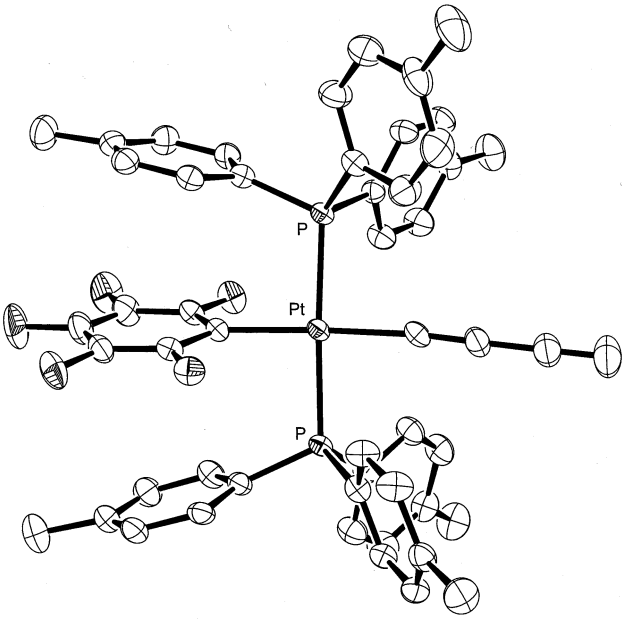


Fig. 4. Molecular structure of *trans*-(C_6F_5)(*p*-$tol_3P)_2PtC{\equiv}CC{\equiv}CH$ (**7**).

tadiynyl) complex **5** and the *p*-tol_3P analog *trans*-(*p*-tol)(*p*-$tol_3P)_2PtC{\equiv}CC{\equiv}CH$ [6] gave only a single weak band at 320–321 nm (ε 3800–2000 $M^{-1}\,cm^{-1}$). Complex **7** was similar (305 nm, ε 5800 $M^{-1}\,cm^{-1}$).

3. Discussion

Three of our model monoplatinum complexes, **3**, **5**, and **7**, feature 1,3-diynyl ligands. This class of compounds has been comprehensively reviewed recently by Low and Bruce [19]. They tabulate eight other platinum(II) bis(1,3-diynyl) complexes with two *mono*phosphine ligands, nearly all of which are *trans* as in **3** and **5**. Only one of these, *trans*-$(n\text{-}Bu_3P)_2Pt(C{\equiv}CC{\equiv}CH)_2$ (**8**; Chart 1) [20], has been crystallographically characterized, as verified by an independent search of the Cambridge data base. We previously reported the similar synthesis and structural characterization of a relevant mono(1,3-butadiynyl) complex, *trans*-(*p*-tol)$(Ph_3P)_2$-$PtC{\equiv}CC{\equiv}CSiMe_3$ (**9**; Chart 1) [8]. For ease of comparison, the key metrical parameters for **8** and **9** are given in Table 2.

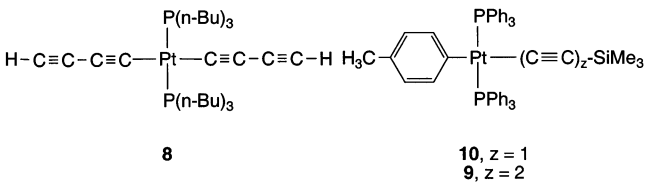
Many platinum(II) alkynyl complexes $L_nPtC{\equiv}CR$ ($R \neq C{\equiv}CR'$) have been characterized crystallographically, and we do not attempt to summarize this literature, for which partial surveys are available [9,21,22]. However, we have determined the crystal structure of *trans*-(*p*-tol)$(Ph_3P)_2PtC{\equiv}CSiMe_3$ (**10**; Chart 1) [8]. Since this represents another obvious reference complex for **2**, **3**, **5**, and **7**, key data are also added to Table 2. All the platinum 1,3-diynyl complexes tabulated by Low and Bruce contain trialkyl or dialkylphenyl-monophosphine

Table 2
Comparison of key bond lengths and angles in monoplatinum complexes

Complex	**2**	**3**	**5**	**7**	**8** [20]	**10** [8]	**9** [8]
Pt–C≡	2.004(3)	2.005(7)	2.009(4)	2.004(3)	1.984(5)	2.035(5)	2.039(15)
Pt–C≡C	1.207(5)	1.201(9)	1.216(6)	1.201(5)	1.211(7)	1.186(7)	1.196(18)
Pt–C≡C–C	–	1.373(9)	1.380(6)	1.381(5)	1.372(8)	–	1.37(2)
Pt–C≡C–C≡C	–	1.206(9)	1.183(7)	1.184(6)	1.159(8)	–	1.196(18)
Pt–P_1	2.3113(8)	2.3108(15)	2.2918(12)	2.3181(7)	2.301(1)	2.2916(13)	2.302(3)
Pt–P_2	2.3113(8)	2.3108(15)	2.2931(12)	2.3027(7)	2.300(2)	2.2998(13)	2.311(3)
Pt–aryl	–	–	2.077(4)	2.060(3)	–	2.057(4)	2.080(13)
C–Pt–C≡	180.00(15)	180.00(16)	176.44(15)	176.81(12)	180.0	176.8(2)	175.2(5)
P_1–Pt–C≡	87.07(9)	85.73(17)	87.14(12)	90.90(9)	91.9(1)	88.11(14)	90.7(4)
P_2–Pt–C≡	92.93(9)	94.27(17)	92.80(13)	87.11(9)	88.2(1)	86.34(14)	93.4(4)
P_1–Pt–P_2	180.0	180.0	178.17(4)	173.98(3)	180.0	174.43(4)	172.45(12)
Pt–C≡C	175.8(3)	177.4(6)	175.9(4)	175.0(3)	178.5(5)	174.2(5)	175.0(11)
Pt–C≡C–X	175.6(3)	178.8(7)	175.6(5)	179.1(5)	176.0(6)	172.3(6)	178.1(14)
Pt–C≡C–C≡C	–	177.8(7)	178.1(6)	179.0(6)	179.4(9)	–	176.8(15)
Pt–C≡C–C≡C–Si	–	171.5(7)	–	–	–	–	174.0(13)

ligands, whereas ours feature triarylphosphines ligands. Trialkylphosphines can displace triarylphosphines from platinum alkynyl complexes [23], and this reactivity mode plays a key role in certain chemical applications of our compounds.

Turning to the data in Table 2, there is a striking similarity of bond lengths and bond angles. The Pt–C≡ distance in the bis(trialkylphosphine) complex **8** is slightly shorter than the others (1.984(5) vs. 2.004(3)–2.035(5) or 2.039(15) Å). The bis(alkynyl) and bis(1,3-diynyl) complexes have linear ≡C–Pt–C≡ linkages (180.0° for **2**, **3**, **8**), whereas the (aryl)Pt(C≡C) complexes have slightly bent C–Pt–C≡ linkages (175.2(5)–176.8(2)° for **5**, **7**, **9**, **10**). Other trends can be identified, but all lengths and angles have the estimated standard deviations. When the difference between the two compounds is less than three times the standard deviations, rigorous conclusions are not possible. However, when parallel differences are noted for a series of compounds, there is additional confidence of a genuine trend. In this context, note that both **2** and **3** give Pt–C≡ distances shorter than the analogs **9** and **10** (2.004(3)–2.005(7) vs. 2.035(5)–2.039(15) Å), implicating an effect of the *trans* ligand upon σ and π interactions. Other such relationships can be seen in Table 2, and are currently being tested by DFT calculations, which often give remarkably accurate bond lengths and angles.



8 **10**, z = 1; **9**, z = 2

Chart 1. Related structurally characterized complexes.

The nature of metal–π interactions in metal–alkynyl complexes has been examined by a number of spectroscopic, structural, and computational probes [21,24]. An analysis of this complicated subject is beyond the scope of this paper. However, photoelectron spectroscopy and DFT calculations indicate modest π acidity, with pronounced interactions between the occupied metal d and ligand π orbitals in 18 valence electron complexes. Sixteen valence electron platinum alkynyl complexes exhibit UV absorptions arising from both π → C≡Cπ* intra-ligand transitions and metal d → C≡Cπ* MLCT transitions [25]. Analogs of **2** which contain donor- and acceptor-substituted phenylalkynyl ligands exhibit NLO properties [22].

Turning to the synthetic aspects of this study, the sequences in Schemes 2 and 3 allow rapid access to a variety of bis(phosphine) complexes of the types *trans*-(*p*-tol)$(R_3P)_2$PtCl and *trans*-$(C_6F_5)(R_3P)_2$PtCl. The yields of most steps are not optimized, and represent realistic outcomes for 'first time' experiments. These complexes are seeing extensive use as precursors to a variety of novel $L_nPt(C{\equiv}C)_zPtL_n$ systems [26], and C_8, C_{12}, and C_{16} complexes derived from **5** and/or **7** have already been reported [6,7]. Protio analogs of the silylated complexes **2** and **3** are precursors to polymers with $[Pt(C{\equiv}C)_z]_y$ repeat units [27]. All these themes as well as the others will be represented in future papers from our laboratory.

4. Experimental

4.1. General

Reactions were conducted under N_2 atmospheres. Commercial chemicals were treated as follows: ether, distilled from Na–benzophenone; $HNEt_2$, distilled from KOH; *p*-tolMgBr (Aldrich, 1.0 M in ether), stan-

dardized [28]; *trans*-$(Ph_3P)_2PtCl_2$ (Aldrich [29]), $HC{\equiv}CSiMe_3$ (Farchan or GFS), CuI (Aldrich, 99.999%), acetyl chloride, and other materials, used as received. IR spectra were recorded in Mattson Polaris FT or ASI ReactIR-1000 spectrometers. UV–vis spectra were recorded on a Shimadzu model 3102 spectrometer. NMR spectra were recorded on standard 300–500 MHz FT spectrometers. Mass spectra were recorded on a Finnigan MAT 95 high-resolution instrument. Microanalyses were conducted by Atlantic Microlab or with a Carlo Erba EA1110 instrument (in-house).

4.2. *trans*-$(Ph_3P)_2Pt(C{\equiv}CSiMe_3)_2$ (2)

A Schlenk flask was charged with *trans*-$(Ph_3P)_2PtCl_2$ (0.500 g, 0.63 mmol) [29], $HNEt_2$ (30 ml), CuI (0.020 g, 0.10 mmol), and $HC{\equiv}CSiMe_3$ (0.270 ml, 2.2 mmol). The suspension was first stirred at 60 °C (0.5 h) and then at room temperature (r.t.) (14 h). The solvent was evaporated under a N_2 stream, and the dark residue taken up in CH_2Cl_2–H_2O. The organic layer was separated, dried ($MgSO_4$), and taken to dryness by rotary evaporation. The residue was taken up in a small amount of $CHCl_3$, and added to 100 ml of rapidly stirred EtOH. The precipitate was isolated on a medium porosity frit and dried under oil pump vacuum to give **2** as a white solid (0.430 g, 0.47 mmol, 74%). Anal. Calc. for $C_{46}H_{48}P_2PtSi_2$: C, 60.46; H, 5.26. Found: C, 60.28; H, 5.24%. IR (cm^{-1}, CH_2Cl_2): $\nu_{C\equiv C}$ 2058 (w, sh), 2038 (s). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.4–7.8 (m, $6C_6H_5$), −0.45 (s, $6CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 135.5 (virtual t, $^2J_{CP} = 6.0$ Hz [11], *o*-Ph), 131.8 (virtual t, $^1J_{CP} = 31.5$ Hz [11], *i*-Ph), 130.3 (s, *p*-Ph), 127.8 (virtual t, $^3J_{CP} = 5.6$ Hz [11], *m*-Ph), 117.8 (s, *C*≡CSi), 58.2 (s, C≡*C*Si), 0.6 (s, $SiCH_3$). $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm): 18.8 (s, $^1J_{PPt} = 2568$ Hz [30a]).

4.3. *trans*-$(Ph_3P)_2Pt(C{\equiv}CC{\equiv}CSiMe_3)_2$ (3)

A Schlenk flask was charged with *trans*-$(Ph_3P)_2PtCl_2$ (0.079 g, 0.10 mmol) [29], $HNEt_2$ (15 ml), CuI (0.006 g, 0.03 mmol), $HC{\equiv}CC{\equiv}CSiMe_3$ (0.061 g, 0.50 mmol) [12], and CH_2Cl_2 (5 ml), and fitted with a condenser. The suspension was stirred at r.t. (3 h) and then 80 °C (oil bath, 2 h). The solvent was removed by rotary evaporation. The dark residue was extracted with toluene (2 × 25 ml). The extract was filtered through alumina (7 cm), and the solvent was removed by rotary evaporation. The residue was suspended in MeOH (5 ml), and the slightly yellow solid collected by filtration and dried by oil pump vacuum to give **3** (0.076 g, 0.079 mmol, 79%), m.p. (dec.) 239–242 °C (decolorization >176 °C). Anal. Calc. for $C_{50}H_{48}P_2Pt$–Si_2: C, 62.42; H, 5.03. Found: C, 61.96; H, 5.39%. IR (cm^{-1}, CH_2Cl_2): $\nu_{C\equiv C}$ 2185 (m), 2131 (s). UV–vis: λ (nm) (ε, $M^{-1}\,cm^{-1}$) (CH_2Cl_2, 1.25×10^{-6} M): 319 (12 000), 339 (26 400). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.75–7.35 (m, $6C_6H_5$), 0.05 (s, $6CH_3$). $^{13}C\{^1H\}$-NMR (δ ppm): 135.2 (virtual t, $^2J_{CP} = 6.0$ Hz [11], *o*-Ph), 130.5 (virtual t, $^1J_{CP} = 29.7$ Hz [11], *i*-Ph), 130.8 (s, *p*-Ph), 128.2 (virtual t, $^3J_{CP} = 5.5$ Hz [11], *m*-Ph), 105.8 (s, *C*≡CC≡CSi), 95.9, 93.5 (2 s, C≡*CC*≡C), 77.7 (s, C≡*C*Si), 0.8 (s, $SiCH_3$). $^{31}P\{^1H\}$-NMR (δ ppm): 18.8 (s, $^1J_{PPt} = 2572$ Hz [30a]).

4.4. (COD)Pt(*p*-tol)$_2$ [14]

A Schlenk flask was charged with $(COD)PtCl_2$ (2.005 g, 5.35 mmol) [14] and ether (30 ml). Then *p*-tolMgBr (1.0 M in ether; 13.4 ml, 13 mmol) was added with stirring. After 16 h, saturated aq. NH_4Cl (25 ml) was added. The ether layer was separated, and the water layer extracted with ether (3 × 50 ml). The combined ether extracts were dried ($MgSO_4$), and filtered through a 1 cm Celite® pad and a 2 cm decolorizing carbon pad. The ether was removed from the filtrate under a N_2 stream. The white solid was suspended in EtOH (25 ml), collected by filtration, and dried by oil pump vacuum to give (COD)Pt(*p*-tol)$_2$ (1.685 g, 3.46 mmol, 65%). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.12 (d, $^3J_{HH} = 10.5$ Hz, $^3J_{HPt} = 67.8$ Hz [30a], 4H/*o* to Pt), 6.85 (d, $^3J_{HH} = 10.3$ Hz, 4H/*m* to Pt), 5.10 (s, $^2J_{HPt} = 24.2$ Hz [30a], $4CH_2CH{=}$), 2.45–2.60 (m, $4CH_2$), 2.18 (s, $2CH_3$).

4.5. (*p*-tol)(COD)PtCl [14]

A Schlenk flask was charged with (COD)Pt(*p*-tol)$_2$ (1.010 g, 2.06 mmol), CH_2Cl_2 (15 ml), and MeOH (15 ml). Acetyl chloride (0.14 ml, 2.0 mmol) was added with stirring. After 15 min, solvent was removed by rotary evaporation. The white residue was suspended in MeOH (15 ml), collected by filtration, and dried by oil pump vacuum to give (*p*-tol)(COD)PtCl (0.660 g, 1.54 mmol, 75% [31]). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.10 (d, $^3J_{HH} = 10.5$ Hz, $^3J_{HPt} = 42.9$ Hz [30a], 2H/*o* to Pt), 6.92 (d, $^3J_{HH} = 10.5$ Hz, 2H/*m* to Pt), 5.80 (m, $^2J_{HPt} = 13.5$ Hz [30a], $2CH_2CH{=}$), 4.60 (m, $^2J_{HPt} = 21$ Hz [30a], $2C'H_2C'H{=}$), 2.30–2.80 (m, $4CH_2$), 2.25 (s, CH_3).

4.6. *trans*-(*p*-tol)$(Ph_3P)_2PtCl$ (4) [13]

A Schlenk flask was charged with (*p*-tol)(COD)PtCl (0.662 g, 1.54 mmol), Ph_3P (0.814 g, 3.10 mmol), and CH_2Cl_2 (30 ml). The mixture was stirred for 16 h. The solvent was removed under a N_2 stream. The white residue was suspended in MeOH (10 ml), collected by filtration, washed with hexanes (5 ml), and dried by oil pump vacuum to give **4** (1.215 g, 1.45 mmol, 94%). Crystallization ($CHCl_3$–MeOH layer–layer diffusion) gave small white needles, m.p. (dec.) 295 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 7.15–7.60 (m, $6C_6H_5$), 6.45 (d, $^3J_{HH} = 12.2$ Hz, $^3J_{HPt} = 50.0$ Hz [30a], 2H/*o* to Pt), 5.95 (d,

$^3J_{HH} = 10.9$ Hz, 2H/*m* to Pt), 1.90 (s, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 136.9 (s, *i* to Pt), 135.0 (virtual t, $^2J_{CP} = 6.0$ Hz [11], *o*-Ph), 130.6 (virtual t, $^1J_{CP} = 27.8$ Hz [11], *i*-Ph), 130.4 (s, *p* to Pt), 123.0 (s, *p*-Ph), 128.9 (s, *o* to Pt), 128.4 (s, *m* to Pt), 127.9 (virtual t, $^3J_{CP} =$ 5.2 Hz [11], *m*-Ph), 20.4 (s, CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm): 24.6 (s, $^1J_{PPt} = 3155$ Hz [30a]).

4.7. *trans*-(*p*-tol)(Ph_3P)$_2$PtC≡CC≡CH (**5**)

A Schlenk flask was charged with **4** (1.500 g, 1.77 mmol), CuI (0.023 g, 0.12 mmol), and $HNEt_2$ (100 ml), and cooled to −45 °C. Then HC≡CC≡CH (2.0 M in THF; 25 ml, 50.0 mmol) [32] was added with stirring. After 1.5 h, the cold bath was removed. After 1 h, solvent was removed by rotary evaporation. The residue was extracted with benzene (2 × 25 ml). The combined extracts were filtered through an alumina column (7 cm). Solvent was removed by rotary evaporation. Ethanol (15 ml) was added, and the pale tan powder was collected by filtration and dried by oil pump vacuum to give **5** (1.422 g, 1.65 mmol, 93%), m.p. (dec.) 182 °C. Anal. Calc. for $C_{47}H_{38}P_2Pt$: C, 65.65; H, 4.45. Found: C, 65.47; H, 4.46%. IR (cm^{-1}, CH_2Cl_2): $\nu_{\equiv CH}$ 3310 (w), $\nu_{C\equiv C}$ 2143 (s). UV-vis: λ (nm) (ε, $M^{-1}\,cm^{-1}$) (CH_2Cl_2, 1.25×10^{-5} M): 321 (3800). MS (positive FAB, 3-NBA/THF, *m*/*z*): 859 (**5**$^+$, 30%), 810 ((tol)(PPh_3)$_2$Pt$^+$, 80%), 719 ((PPh_3)$_2$Pt$^+$, 100%); no other peaks above 400 of > 3%. ^{1}H-NMR ($CDCl_3$, δ ppm): 7.51–7.24 (m, $6C_6H_5$), 6.34 (d, $^3J_{HH} = 7.8$ Hz, $^3J_{HPt} = 55.3$ Hz [30a], 2H/*o* to Pt), 6.08 (d, $^3J_{HH} = 7.5$ Hz, 2H/*m* to Pt), 1.92 (s, CH_3), 1.41 (t, $J_{HP} = 0.9$ Hz, ≡CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 149.9 (s, *i* to Pt), 139.5 (s, *o* to Pt), 135.4 (virtual t, $^2J_{CP} = 6.1$ Hz [11], *o*-Ph), 131.6 (virtual t, $^1J_{CP} = 28.7$ Hz [11], *i*-Ph), 130.5 (s, *p*-Ph), 130.3 (s, *p* to Pt), 128.8 (s, *m* to Pt), 128.3 (virtual t, $^3J_{CP} = 5.4$ Hz [11], *m*-Ph), 110.7 (s, Pt*C*≡C) [30b,33], 96.3 (s, PtC≡*C*) [33], 73.3 (s, *C*≡CH) [33], 59.2 (s, C≡*C*H) [33], 21.1 (s, CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm): 21.3 (s, $^1J_{PPt} = 2959$ Hz [30a]).

4.8. *trans*-(C_6F_5)(*p*-tol_3P)$_2$PtCl (**6**)

A Schlenk flask was charged with [Pt(C_6F_5)(SR_2)(μ-Cl)]$_2$ (0.729 g, 0.750 mmol; SR_2 = tetrahydrothiophene) [17], *p*-tol_3P (1.029 g, 3.381 mmol), and CH_2Cl_2 (25 ml). The solution was stirred for 16 h and filtered through a Celite®–decolorizing carbon–glass frit assembly. The solvent was removed by rotary evaporation. The residue was washed with methanol (2 × 15 ml) and dried by oil pump vacuum to give **6** as a white powder (1.410 g, 1.401 mmol, 93%), m.p. (dec) > 230 °C. Anal. Calc. for $C_{48}H_{42}ClF_5P_2Pt$: C, 57.29; H, 4.21. Found: C, 57.29; H, 4.34%. MS (positive FAB, 3-NBA, *m*/*z*): 1005 (**6**$^+$, 5%), 970 ((C_6F_5)(tol_3P)$_2$Pt$^+$, 20%), 802 ((tol_3P)$_2$Pt$^+$, 23%), 497 ((tol_3P)Pt$^+$, 8%), 304 (100) (tol_3P^+, 100%). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.51 (m, 12H/*o* to P), 7.09 (d, $^3J_{HH} = 7.8$ Hz, 12H/*m* to P), 2.33 (s, $6CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 145.2 (dd, $^1J_{CF} = 225$ Hz, $^2J_{CF} = 21$ Hz, *o* to Pt), 140.7 (s, *p* to P), 136.9 (dm, $^1J_{CF} = 241$ Hz, *p* to Pt), 136.2 (dm, $^1J_{CF} =$ 245 Hz, *m* to Pt), 134.4 (virtual t, $^2J_{CP} = 6.5$ Hz [11], *o* to P), 128.7 (virtual t, $^3J_{CP} = 6.0$ Hz [11], *m* to P), 126.6 (virtual t, $^1J_{CP} = 29.7$ Hz [11], *i* to P), 21.3 (s, CH_3). $^{31}P\{^1H\}$-NMR (δ ppm): 19.9 (s, $^1J_{PPt} = 2728$ Hz [30a]).

4.9. *trans*-(C_6F_5)(*p*-tol_3P)$_2$PtC≡CC≡CH (**7**)

A Schlenk flask was charged with **6** (1.560 g, 1.550 mmol), CuI (0.060 g, 0.32 mmol), CH_2Cl_2 (10 ml), and $HNEt_2$ (100 ml), and cooled to −45 °C. Then HC≡CC≡CH (2.9 M in THF; 8.6 ml, 24.9 mmol) [32] was added with stirring. The cold bath was allowed to warm to r.t. (ca. 3 h). After an additional 2.5 h, the solvent was removed by oil pump vacuum. The residue was extracted with toluene (3 × 20 ml). The combined extracts were filtered through an alumina column (7 cm). The solvent was removed by rotary evaporation. Ethanol (20 ml) was added, and the off-white solid was collected by filtration and dried by oil pump vacuum to give **7** (1.275 g, 1.250 mmol, 81%), m.p. (dec.) > 171 °C. Anal. Calc. for $C_{52}H_{43}F_5P_2Pt$: C, 61.24; H, 4.25. Found: C, 60.83; H, 4.31% IR (cm^{-1}, powder film): $\nu_{\equiv CH}$ 3320 (w), $\nu_{C\equiv C}$ 2154 (m). UV–vis: λ (nm) (ε, $M^{-1}\,cm^{-1}$) (CH_2Cl_2, 1.25×10^{-5} M): 305 (5800). MS (positive FAB, 3-NBA, *m*/*z*): 1020 (**7**$^+$, 26%), 970 ((C_6F_5)(tol_3P)$_2$Pt$^+$, 72%), 851 ((tol_3P)$_2$PtC≡CC≡CH$^+$, 23%), 803 ((tol_3P)$_2$Pt$^+$, 100%). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.49 (m, 12H/*o* to P), 7.10 (d, $^3J_{HH} = 7.4$ Hz, 12H/*m* to P), 2.34 (s, $6CH_3$), 1.46 (s, ≡CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 145.8 (dd, $^1J_{CF} = 224$ Hz, $^2J_{CF} = 22$ Hz, *o* to Pt), 140.7 (s, *p* to P), 136.8 (dm, $^1J_{CF} = 239$ Hz, *p* to Pt), 136.3 (dm, $^1J_{CF} = 248$ Hz, *m* to Pt), 134.3 (virtual t, $^2J_{CP} = 6.2$ Hz [11], *o* to P), 128.6 (virtual t, $^3J_{CP} = 5.2$ Hz [11], *m* to P), 127.4 (virtual t, $^1J_{CP} = 30.2$ Hz [11], *i* to P), 97.8 (s, $^1J_{CPt} = 990$ Hz, Pt*C*≡C) [30a,33], 94.9 (s, $^1J_{CPt} = 266$ Hz, PtC≡*C*) [30a,33], 72.5 (s, *C*≡CH) [33], 59.6 (s, C≡*C*H) [33], 21.3 (s, CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm): 17.6 (s, $^1J_{PPt} = 2655$ Hz [30a]).

4.10. Crystallography

A concentrated benzene solution of **2** was carefully layered with EtOH. After 2 weeks, long colorless needles were obtained. Data were collected as outlined in Table 1. Cell parameters (200(0.1) K) were obtained from ten frames using a 10° scan. The space group was determined from least-squares refinement. Lorentz, polarization, and absorption corrections were applied using DENZO-SMN and SCALEPACK [34]. The structure was solved by standard heavy atom techniques with the

SIR97 package and refined with SHELXL-97 [35]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, using the riding model.

A concentrated benzene solution of **3** was layered with EtOH. After 1 week, a single large irregular prism had formed. Data were collected using a piece of this crystal. The cell parameters and space group were determined as for **2**. An identical refinement led to a unit cell containing an EtOH molecule, the CH_2OH group of which showed displacement disorder (C45S, O1S) that could be refined to a 50:50 occupancy ratio. A concentrated 1,2 dichloroethane solution of **5** was layered with hexanes. After 2 weeks, small light yellow prisms were obtained. Cell parameters (291(2) K) were obtained from 25 reflections with $13° < 2\theta < 14°$. The data were refined as in the previous two cases. A $CHCl_3$ solution of **7** was layered with EtOH. After 1 week, irregular, off-white prisms were obtained. The cell parameters and space group were determined, and corrections applied, as for **2**. The structure was solved by direct methods, and refined as for **2**. In all cases, scattering factors were taken from the literature [36].

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 162672, 162673, 134343 and 168536 for **2**, **3**·ethanol, **5** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[30] (a) This coupling represents a satellite (d; $^{195}Pt = 33.8\%$), and is not reflected in the peak multiplicity given;
(b) A satellite would be expected based upon other spectra in this paper, but could not be discerned above background noise.

[31] Alternatively, this procedure can be conducted with 1.7 equivalents of acetyl chloride (0.5 h reaction time), giving a 94% yield. However, if the reaction is allowed to proceed too long, or acetyl chloride is used in greater excess (COD)$PtCl_2$ forms. The relative amounts of (COD)Pt(p-tol)$_2$, *trans*-(p-tol)(COD)Pt(p-tol), and (COD)$PtCl_2$ are easily assayed by ^{1}H-NMR.

[32] The HC≡CC≡CH concentration is calculated from the mass increase of the THF solution [16]. CAUTION: this compound is explosive and literature precautions should be followed.

[33] These signals are assigned by analogy to those of the more soluble p-tol$_3$P analog, for which additional diagnostic couplings (J_{CP}, J_{CPt}) could be observed and ^{1}H-undecoupled spectra were recorded [6].

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