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Reactivity of Dipyridyl Ditellurides with (Diphosphine)Pt^0 and 2-Pyridyltellurolates with (Diphosphine)PtCl$_2$ and Isolation of Different Structural Motifs of Platinum(II) Complexes

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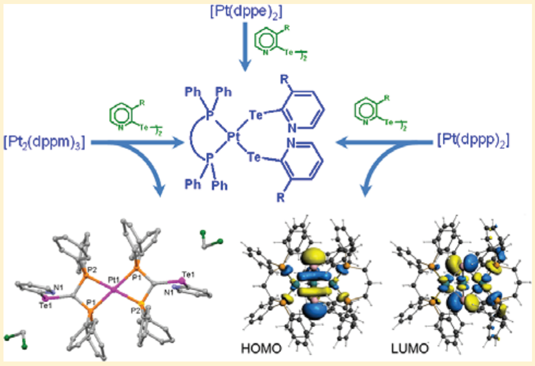
Supporting Information



ABSTRACT: Oxidative addition reaction of dipyridyl ditellurides to [Pt$_2$(dppm)$_3$] gave two types of complexes, [Pt{2-Te-C$_5$H$_3$(3-R)N}$_2$(dppm)] (**1**) and [Pt{PPh$_2$C(TeC$_5$H$_3$(3-R)N)$_2$PPh$_2$}$_2$] (**2**) (R = H or Me), in ~65 and ~20% yield, respectively. Both these complexes are also formed in the substitution reaction between [PtCl$_2$(dppm)] and NaTeC$_5$H$_3$(3-R)N. Treatment of [Pt(dppe)$_2$] with dipyridyl ditellurides yielded an oxidative addition product, [Pt{2-Te-C$_5$H$_3$(3-R)N}$_2$ (dppe)] (**3**) (R = H or Me), exclusively. In a substitution reaction of [PtCl$_2$(dppe)] with NaTeC$_5$H$_3$(3-Me)N a complex of composition Pt{TeC$_5$H$_3$(3-Me)N}(dppe)Cl (**4**) was formed. The reaction between either [Pt(dppp)$_2$] and Te$_2$(C$_5$H$_3$(3-Me)N)$_2$ or [PtCl$_2$(dppp)] and NaTeC$_5$H$_3$(3-R)N afforded a mixture of [Pt{2-Te-C$_5$H$_3$(3-Me)N}$_2$(dppp)] (**5**) and [Pt$_3$Te$_2$(dppp)$_3$]$^{2+}$ (**6**), which were separated by column chromatography. All the complexes were characterized by elemental analyses and NMR (^{1}H, ^{31}P, ^{195}Pt) spectroscopy. The molecular structures of [Pt{PPh$_2$C(TeC$_5$H$_4$N)$_2$PPh$_2$}$_2$] and [Pt$_2${TeC$_5$H$_3$(3-Me)N}$_2$(dppe)$_2$][BPh$_4$]$_2$ were established by single-crystal X-ray diffraction analyses. The bonding, charge transfer, and geometry of compounds [Pt{2-Te-C$_5$H$_3$(3-R)N}$_2$(dppm)] (**1**), [Pt{PPh$_2$C(TeC$_5$H$_3$(3-R)N)$_2$PPh$_2$}$_2$] (**2**), and [Pt$_3$Te$_2$(dppp)$_3$]$^{2+}$ (**6**) have been analyzed through relativistic density functional calculations.

INTRODUCTION

Oxidative addition reactions of E−X (E = heteroatom, X = H,[1] C,[2] or heteroatom[3,4]) to zerovalent group 10 metal complexes have attracted considerable attention for quite some time.[5] The remarkable reactivity of Ni^0 and Pd^0 has been used in synthetic chemistry, as their reactions, in general, give high product yield with great selectivity under mild conditions.[6] Not only are these complexes used as precursors, but several of them are envisaged as active species in catalytic reactions. The corresponding platinum(0) complexes, on the other hand, due to their superior stability, provide an opportunity to understand the mechanistic details and learn about the nature of complexes involved in such reactions.[7]

Oxidative addition reaction of diorgano-disulfides and -diselenides to zerovalent group 10 metals is of much current interest.[4,8−10] The reaction has been employed for the synthesis of vinylsulfides and vinylselenides by E−E addition to C≡C bonds of acetylenic hydrocarbons.[4,11] Such addition reactions proceed in a regio- and stereoselective manner with almost 100% atom efficiency.[4] During oxidative addition reactions, the chalcogen−chalcogen bond is reductively cleaved with concomitant formation of two metal−chalcogenolate bonds under relatively mild conditions. The resulting complexes find application in organic synthesis[12] and materials science.[13] These reactions with Pd(0) species, in general, afford binuclear complexes (e.g., [Pd$_2$(ER)$_2$(μ-ER)$_2$(PR'$_3$)$_2$]), whereas the corresponding platinum(0) derivatives yield mononuclear complexes (e.g., [Pt(ER)$_2$(PR'$_3$)$_2$] (E = S or Se)).[9] In contrast, oxidative addition reactions of diorgano ditellurides with Pd(0) and Pt(0) are often more complex, yielding several products.[14,15] Some of these products, e.g., [Pd$_6$Te$_4$(TePh)$_4$(PPh$_3$)$_6$] and [Pt$_3$Te$_2$(Th)(PPh$_3$)$_5$]Cl,[14] are formed by competitive cleavage of Te−Te and Te−C bonds. The distinct reactivity of tellurium ligands may be attributed to comparable bond energies of Te−Te and Te−C bonds and increased metallic character of Te from lighter chalcogens (S or Se). Recent theoretical calculations by Morokuma et al. on oxidative addition of an E−E bond to Pd(0) and Pt(0) have revealed that the M−TeR bond energy is the lowest in [Pt(ER)$_2$(PR'$_3$)$_2$] (E = S, Se or Te) complexes and the Pt−ER bond is stronger than the Pd−ER linkage.[9] It has also been shown that the transition state involving activation of RE−ER by M^0(PR$_3$)$_2$ species requires deformation in the P−M−P angle.[9]

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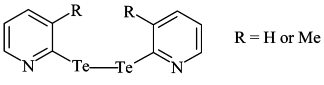
Pyridyl tellurolates are hemilabile ligands and can bind metal atoms in different ways, viz., through a tellurium atom, through a nitrogen atom, or in a bidentate mode (Te$^\cap$N; chelating or bridging). Unlike simple tellurolate ligands (e.g., $PhTe^-$), the presence of both hard (N) and soft (Te) atoms in the pyridyl tellurolate ligand may contribute to the reactivity and overall stability of the resulting complexes. Recently we have reported the formation of a serendipitous product, $[Pt(Te)(TeAr)_2(PPh_3)]$ (Ar = C_5H_4N and $C_5H_3(Me)N$), containing bare Te^0 coordinated to platinum(II), together with the expected products, $[Pt(TeAr)_2(PPh_3)_2]$, in the reactions of $[Pt(PPh_3)_4]$ with dipyridyl ditellurides.[15] We have now chosen platinum(0) complexes containing chelating diphosphines with varying degree of P−M−P angles and studied their oxidative addition reactions with dipyridyl ditellurides (**I**). Depending on the nature of the diphosphine ligand, different products could be isolated. The results of this work are reported herein.



I

EXPERIMENTAL SECTION

The compounds $[PtCl_2(P^\cap P)]$ ($P^\cap P$ = dppm, dppe, dppp),[16] $[Pt_2(dppm)_3]$,[17] $[Pt(P^\cap P)_2]$ ($P^\cap P$ = dppe, dppp),[18] $(C_5H_4N)_2Te_2$, and $(3\text{-}MeC_5H_3N)_2Te_2$[19] were prepared according to literature methods. Tertiary phosphines were procured from Strem Chemicals. All reactions were carried out under an argon/nitrogen atmosphere in dry and distilled analytical grade solvents at room temperature. The ^1H, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker Avance-II spectrometer operating at 300, 121.49, and 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform (δ 7.26) for ^1H, external 85% H_3PO_4 for ^{31}P, and Na_2PtCl_6 in D_2O for ^{195}Pt. Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer. The conductivity measurements were carried out on a EUTECH-CON 1500 conductivity meter.

Intensity data for $[Pt\{PPh_2C(TeC_5H_4N)_2PPh_2\}_2]\cdot 2CH_2Cl_2$ ($\mathbf{2a}\cdot 2CH_2Cl_2$) and $[Pt_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2]\cdot[BPh_4]_2$ (**4b**) were measured on Rigaku AFC 7S and Bruker Apex-II CCD diffractometers, respectively, with Mo Kα radiation so that θ_{max} = 27.5°. The structures were solved by direct methods,[20] and refinement[21] was on F^2 using data that had been corrected for absorption effects with an empirical procedure. Non-hydrogen atoms were modeled with anisotropic displacement parameters, with hydrogen atoms in their calculated positions. Molecular structures were drawn using ORTEP.[22] Crystallographic and structural determination data are listed in Table 1.

(i) **Syntheses of Complexes.** *$[Pt(2\text{-}Te\text{-}C_5H_4N)_2(dppm)]$ (**1a**) and $[Pt\{PPh_2C(TeC_5H_4N)_2PPh_2\}_2]$ (**2a**).* To a toluene solution ($10\ cm^3$) of $(C_5H_4N)_2Te_2$ (98 mg, 0.24 mmol) was added a solution ($30\ cm^3$) of $[Pt_2(dppm)_3]$ (175 mg, 0.11 mmol) in the same solvent with stirring, which continued for 4 h at room temperature. The supernatant was decanted, and the orange precipitate was washed thoroughly with hexane and diethyl ether and dried under vacuum to afford a yellow powder, $[Pt(2\text{-}Te\text{-}C_5H_4N)_2(dppm)]$ (**1a**) [(yield 75 mg, 67%; mp 163 °C (dec)) Anal. Calcd for $C_{35}H_{30}N_2P_2PtTe_2$: C, 42.42; H, 3.05; N, 2.82. Found: C, 42.17; H, 3.23; N, 2.52. ^1H NMR ($CDCl_3$) δ: 4.40 (t, ^2J(P−H) = 10 Hz, ^3J(Pt−H) = 53 Hz); 6.57 (d); 6.76 (dt, 1.8 Hz d, 7.5 Hz (t) (C_5H_4N)); 7.09−7.79 (m, Ph); 8.04 (d, 7.8 Hz, C_5H_4N); 8.46 (dd, 1, 4 Hz, C_5H_4N). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −53.0 (^1J(Pt−P) = 2547 Hz)]. The supernatant was passed through a Florisil column, and the filtrate was dried under reduced pressure to give an orange powder, $[Pt\{PPh_2C(TeC_5H_4N)_2PPh_2\}_2]$ (**2a**) (yield 32 mg, 21%, mp 48 °C). Anal. Calcd for $C_{60}H_{48}N_2P_4PtTe_2$: C, 52.55; H, 3.53; N, 2.04. Found: C, 52.19; H, 3.65; N, 2.35. ^1H NMR ($CDCl_3$) δ: 7.02 (dd, C_5H_4N); 7.04−7.74 (m, Ph); 8.04 (d, 7 Hz, C_5H_4N); 8.45 (d, 1.8 Hz, C_5H_4N). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −29.3 (^1J(Pt−P) = 1909 Hz).

Table 1. Crystallographic and Structural Determination Data for $[Pt\{PPh_2C(TeC_5H_4N)_2PPh_2\}_2]\cdot 2CH_2Cl_2$ ($\mathbf{2a}\cdot 2CH_2Cl_2$) and $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2]\cdot[BPh_4]_2$ (4b)

	$\mathbf{2a}\cdot 2CH_2Cl_2$	**4b**
chemical formula	$C_{60}H_{48}N_2P_4PtTe_2\cdot 2CH_2Cl_2$	$C_{112}H_{100}B_2N_2P_4Pt_2Te_2$
fw	1541.03	2264.82
cryst size (mm^3)	0.30 × 0.30 × 0.20	0.32 × 0.25 × 0.10
cryst syst	monoclinic	monoclinic
temperature (K)	298	100
space group	$P2_1/n$	$C2/c$
unit cell dimensions		
a (Å)	19.740(4)	30.256(4)
b (Å)	13.033(2)	16.828(2)
c (Å)	11.766(2)	22.048(5)
β (deg)	90.618(15)	123.007(2)
volume ($Å^3$)	3026.7(10)	9414(3)
ρ_{calcd} ($g\ cm^{-3}$)	1.691	1.598
Z	2	4
μ (mm^{-1})/F(000)	3.585/1496	3.695/4464
limiting indices	$-25 \leq h \leq 25$	$-36 \leq h \leq 36$
	$0 \leq k \leq 16$	$-20 \leq k \leq 20$
	$-15 \leq l \leq 8$	$-21 \leq l \leq 26$
θ for data collection (deg)	2.54 to 27.50	2.90 to 25.44
no. of reflns collected	6934	8487
no. of independent reflns	4975	6503
data/restraints/params	6934/1/340	8487/0/560
final R_1, wR_2 indices	0.0514/0.1267	0.0287/0.0599
R_1, wR_2 (all data)	0.0857/0.1478	0.0475/0.0666
goodness of fit on F^2	1.040	1.017

(ii) To a dichloromethane solution ($14\ cm^3$) of $[PtCl_2(dppm)]$ (110 mg, 0.17 mmol) was added a methanol−benzene solution ($10\ cm^3$) of $Na(2\text{-}Te\text{-}C_5H_4N)$ [freshly prepared from $(C_5H_4N)_2Te_2$ (72 mg, 0.17 mmol) in benzene and $NaBH_4$ (13.4 mg, 0.35 mmol) in methanol]. The mixture was stirred for 5 h, whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether. The product was extracted with dichloromethane, filtered, and passed through a Florisil column. The resulting solution was concentrated ($5\ cm^3$) under vacuum, and hexane ($0.5\ cm^3$) was added, which on refrigeration at −5 °C afforded two different products, viz., orange crystals of $[Pt\{PPh_2C(TeC_5H_4N)_2PPh_2\}_2]$ (**2a**) [(yield 104 mg, 45%, mp 48 °C) Anal. Calcd for $C_{60}H_{48}N_2P_4PtTe_2\cdot CH_2Cl_2$: C, 50.31; H, 3.46; N, 1.92. Found: C, 49.78; H, 3.52; N, 1.56. ^1H NMR ($CDCl_3$) δ: 6.82 (d, C_5H_4N), 7.05 (m, Ph), 7.40 (dd, C_5H_4N 2H), 7.68 (br, Ph), 8.04 (m, Ph + C_5H_4N 2H), 8.46 (d, C_5H_4N). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −29.3 (^1J(Pt−P) = 1909 Hz)], and a yellow powder, $[Pt(2\text{-}Te\text{-}C_5H_4N)_2(dppm)]$ (**1a**) [(yield 46 mg, 25%; mp 163 °C (dec)) Anal. Calcd for $C_{35}H_{30}N_2P_2PtTe_2$: C, 42.42; H, 3.05; N, 2.82. Found: C, 42.58; H, 3.08; N, 3.42. ^1H NMR ($CDCl_3$) δ: 4.40 (m, dppm $-PCH_2$), 7.05 (d, 7.8 Hz, C_5H_4N), 7.13−7.80 (m, Ph), 8.45 (d, C_5H_4N 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −53.0 (^1J(Pt−P) = 2552 Hz)], which were separated manually.

(i) *$[Pt\{2\text{-}Te\text{-}C_5H_3(3\text{-}Me)N\}_2(dppm)]$ (**1b**) and $[Pt\{PPh_2C(TeC_5H_3(3\text{-}Me)N)_2PPh_2\}_2]$ (**2b**).* Prepared similarly to the above method (i) and recrystallized from benzene−hexane, which afforded an orange powder, [Pt{PPh$_2$C(TeC$_5$H$_3$(3-Me)N)$_2$PPh$_2$}$_2$] (**2b**) [(yield 24 mg, 18%; mp 110 °C (dec)) Anal. Calcd for $C_{62}H_{52}N_2P_4PtTe_2$: C, 53.21; H, 3.74; N, 2.00. Found: C, 53.10; H, 3.78; N, 1.97. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: −25.1 (^1J(Pt−P) = 1903 Hz)], and a yellow powder, [Pt{2-Te-C$_5$H$_3$(3-Me)N}$_2$(dppm)] (**1b**) [(yield 39 mg, 62%; mp 170 °C (dec)) Anal. Calcd for $C_{37}H_{34}N_2P_2PtTe_2$: C, 43.61; H, 3.36; N, 2.75. Found: C, 43.89; H, 3.34; N, 2.64. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: −51.9 [^1J(Pt−P) = 2615 Hz].

(ii) Prepared in a similar fashion adopting method (ii), and the crude product was extracted with benzene and recrystallized from a benzene−hexane mixture to afford an orange powder, [Pt{PPh$_2$C(TeC$_5$H$_3$(3-Me)N)$_2$PPh$_2$}$_2$] (**2b**) [(yield 22%; mp 110 °C (dec)) Anal. Calcd for $C_{62}H_{52}N_2P_4PtTe_2$: C, 53.21; H, 3.74; N, 2.00. Found: C, 52.80; H, 3.43; N 1.71. ^{1}H NMR (CDCl$_3$) δ: 2.44 (s, Me), 7.06 (d, C$_5$H$_3$N 2H), 7.18(m, Ph), 7.30 (d, C$_5$H$_3$N 2H), 7.36 (q, Ph), 7.49(m, Ph), 7.65(dd, C$_5$H$_3$N 2H), 7.69(br, Ph), 8.31(d, C$_5$H$_3$N 2H). ^{31}P{^{1}H} NMR (CDCl$_3$) δ: −25.6 (^1J(Pt−P) = 1913 Hz)], and the benzene-insoluble part of the crude product, which was extracted in dichloromethane and recrystallized from a dichloromethane−diethyl ether mixture to give a yellow powder, [Pt{2-Te-C$_5$H$_3$(3-Me)N}$_2$(dppm)] (**1b**) (yield 58%; mp 170 °C (dec)). Anal. Calcd for $C_{37}H_{34}N_2P_2PtTe_2$: C, 43.61; H, 3.36; N, 2.75. Found: C, 43.52; H, 3.68; N, 2.42. ^{1}H NMR (CDCl$_3$) δ: 2.44 (s, Me), 3.16 (d, dppm −PCH$_2$), 6.92 (dd, C$_5$H$_3$N 2H), 7.28 (br, Ph), 7.43 (d, C$_5$H$_3$N 2H), 7.71 (br, Ph), 7.93 (dd, C$_5$H$_3$N 2H), 8.25 (d, C$_5$H$_3$N 2H). ^{31}P{^{1}H} NMR (CDCl$_3$) δ: −51.9 [^1J(Pt−P) = 2632 Hz]. ^{195}Pt{^{1}H} NMR (CDCl$_3$) δ: −4712 (^1J(Pt−P) = 2650 Hz).

(i) *[Pt(2-Te-C$_5$H$_4$N)$_2$(dppe)] (**3a**).* To a benzene solution (12 cm^3) of (C$_5$H$_4$N)$_2$Te$_2$ (54 mg, 0.13 mmol) was added a solution (30 cm^3) of [Pt(dppe)$_2$] (125 mg, 0.13 mmol) in the same solvent with stirring, which continued for 3 h at room temperature. The solvent was evaporated under vacuum, and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated dppe. The residue was recrystallized from a benzene−hexane mixture to afford a yellow powder (yield 86 mg, 68%, mp 178 °C (dec)). Anal. Calcd for $C_{36}H_{32}N_2P_2PtTe_2$: C, 43.03; H, 3.21; N, 2.79. Found: C, 43.51; H, 3.07; N 2.96. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 46.1 [^1J(Pt−P) = 2894 Hz].

(ii) To a benzene suspension (15 cm^3) of [PtCl$_2$(dppe)] (100 mg, 0.15 mmol) was added a methanolic solution (12 cm^3) of Na(2-Te-C$_5$H$_4$N) [freshly prepared from (C$_5$H$_4$N)$_2$Te$_2$ (62 mg, 0.15 mmol) in benzene and NaBH$_4$ (13 mg, 0.34 mmol) in methanol]. The mixture was stirred for 3 h, whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether. The product was extracted with acetone and passed through a Florisil column. To the resulting solution was added hexane to precipitate the title complex as an orange powder (yield 98 mg, 65%, mp 178 °C (dec)). Anal. Calcd for $C_{36}H_{32}N_2P_2PtTe_2 \cdot CH_2Cl_2$: C, 40.78; H, 3.14; N, 2.57. Found: C, 41.20; H, 3.29; N, 2.30. ^{1}H NMR (CDCl$_3$) δ: 2.10 (m, dppe 6H), 6.63 (d, C$_5$H$_4$N 2H), 6.72 (t, C$_5$H$_4$N), 7.30−7.35 (m, Ph), 7.84 (d, 3.6 Hz, C$_5$H$_4$N). ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 46.1 [^1J(Pt−P) = 2887 Hz]. ^{195}Pt{^{1}H} NMR (CDCl$_3$) δ: −5346 [^1J(Pt−P) = 2914 Hz].

*[Pt{2-Te-C$_5$H$_3$(3-Me)N}$_2$(dppe)] (**3b**).* To a benzene solution (10 cm^3) of {C$_5$H$_3$(3-Me)N}$_2$Te$_2$ (48 mg, 0.11 mmol) was added a solution (30 cm^3) of [Pt(dppe)$_2$] (110 mg, 0.11 mmol) in the same solvent with stirring, which continued for 4 h at room temperature. The solvent was evaporated under vacuum, and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated dppe. The residue was recrystallized from a benzene−hexane mixture to afford a yellow powder (yield 81 mg, 71%, mp 185 °C (dec)). The characterization data are consistent with the literature values.[23]

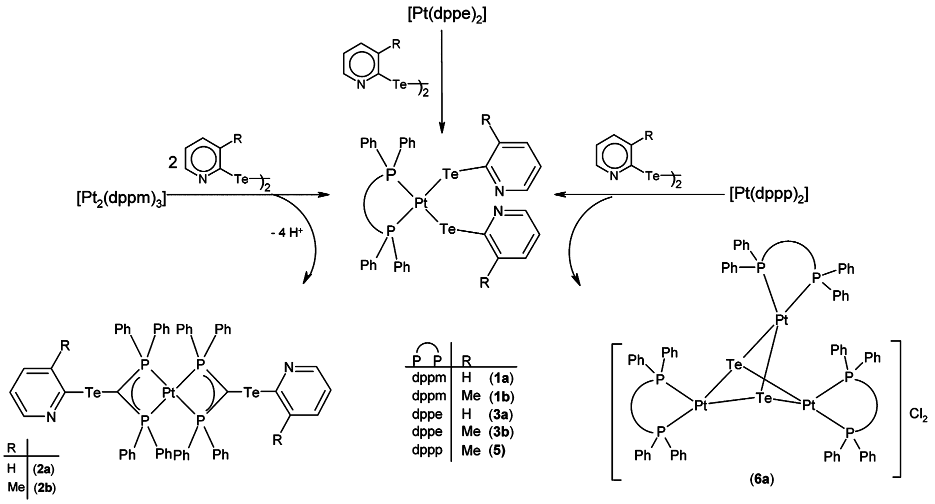
*Pt{TeC$_5$H$_3$(3-Me)N}(dppe)Cl (**4a**).* To a benzene suspension (13 cm^3) of [PtCl$_2$(dppe)] (110 mg, 0.17 mmol) was added a methanolic solution (8 cm^3) of Na{2-Te-C$_5$H$_3$(3-Me)N} [freshly prepared from {C$_5$H$_3$(3-Me)N}$_2$Te$_2$ (74 mg, 0.17 mmol) in benzene and NaBH$_4$ (13.7 mg, 0.36 mmol)]. The mixture was stirred for 3 h, whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether. The product was extracted with acetone, filtered, and passed through a Florisil column. To the resulting solution was added hexane to yield an orange powder of Pt{TeC$_5$H$_3$(3-Me)N}(dppe)Cl (**4a**) (yield 104 mg, 74%, mp 193 °C (dec)). Anal. Calcd for $C_{64}H_{60}N_2Cl_2P_4Pt_2Te_2$: C, 45.28; H, 3.56; N, 1.65. Found: C, 45.68; H, 3.62; N, 1.91. Conductivity measurements (μS cm^2 mol^{-1}): 3.0 (CHCl$_3$), 70.6 (CH$_3$CN), 83.3 (CH$_3$OH). ^{1}H NMR (CDCl$_3$) δ: 2.09 (s, Me), 2.86 (br, dppe −CH$_2$), 6.70 (m, C$_5$H$_3$(3-Me)N), 7.00 (m), 7.36 −7.87 (m, Ph), 8.24 (d, C$_5$H$_3$(3-Me)N). ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 41.9 [^1J(Pt−P) = 2940 Hz], 36.7 [^1J(Pt−P) = 3267 Hz].

To prepare good-quality crystals, a larger anion, Ph$_4$B$^-$, was used. Thus during the reaction, an acetone solution of NaBPh$_4$ (113 mg, 0.33 mmol) was added to the reaction mixture and stirred for 2 h. The whole solution was centrifuged for 10 min. The supernatant was decanted and dried under vacuum to afford an orange powder, which was recrystallized from an acetone−diethyl ether mixture to yield orange crystals of [Pt$_2${TeC$_5$H$_3$(3-Me)N}$_2$(dppe)$_2$](BPh$_4$)$_2$ (**4b**) (yield 80 mg, mp 205 °C (dec)). Characterization data are consistent with the reported ones.[23]

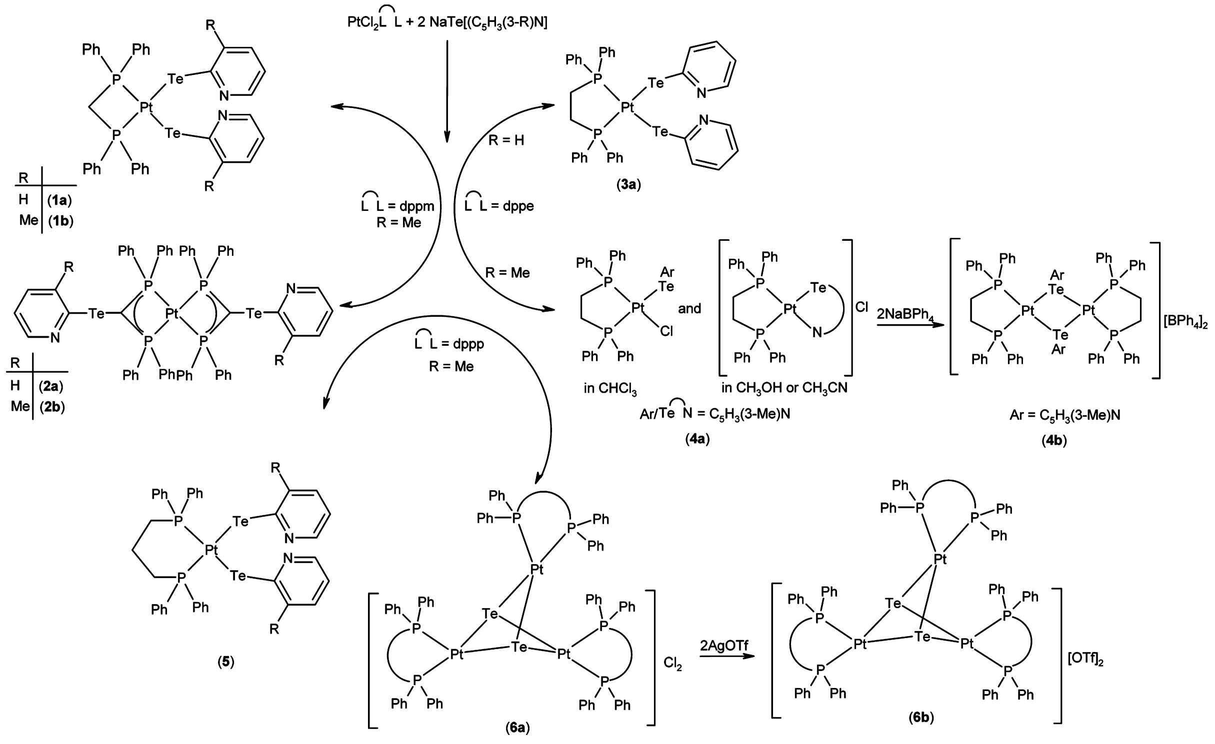
(i) *[Pt{2-Te-C$_5$H$_3$(3-Me)N}$_2$(dppp)] (**5**) and [Pt$_3$Te$_2$(dppp)$_3$]Cl$_2$ (**6a**).* To an acetone solution (15 cm^3) of [PtCl$_2$(dppp)] (97 mg, 0.14 mmol) was added a methanolic solution (12 cm^3) of Na{2-Te-C$_5$H$_3$(3-Me)N} [freshly prepared from {C$_5$H$_3$(3-Me)N}$_2$Te$_2$ (69 mg, 0.16 mmol) in benzene and NaBH$_4$ (11.8 mg, 0.31 mmol)]. The mixture was stirred for 4 h, whereupon a clear orange solution was obtained. The solvents were evaporated under vacuum. The residue was washed thoroughly with hexane followed by diethyl ether and dried under reduced pressure. The crude product was purified by column chromatography (neutral and active aluminum oxide), eluting with a benzene−diethyl ether mixture, from which a yellow powder was obtained, [Pt{2-Te-C$_5$H$_3$(3-Me)N}$_2$(dppp)] (**5**) (yield 58 mg, 39%, mp 147 °C (dec)). Anal. Calcd for $C_{39}H_{38}N_2P_2PtTe_2$: C, 44.74; H, 3.66 N, 2.67. Found: C, 44.36; H, 3.96 N, 2.54. ^{1}H NMR (CDCl$_3$) δ: 1.86 (s, Me); 2.52 (br); 3.04−3.15 (m) CH$_2$; 6.45−7.79 (m, Ph + C$_5$H$_3$N). ^{31}P{^{1}H} NMR (CDCl$_3$) δ: −10.3 (^1J(Pt−P) = 2740 Hz). After separation of **5**, the column was run using a benzene−chloroform mixture (4:1 v/v), giving an orange powder of [Pt$_3$Te$_2$(dppp)$_3$]Cl$_2$ (**6a**) (yield 107 mg, 35%, mp 169 °C). Anal. Calcd for $C_{81}H_{78}Cl_2P_6Pt_3Te_2$: C, 45.28; H, 3.66. Found: C, 45.26; H, 3.96. To this was added a solution of AgSO$_3$CF$_3$ (73 mg, 28 mmol) with stirring, which continued for 1 h at room temperature. The contents were centrifuged for 5 min. The supernatant was decanted, filtered, and dried under vacuum to afford a brown powder, which was recrystallized from a chloroform−diethyl ether mixture to yield yellowish-brown crystals of [Pt$_3$Te$_2$(dppp)$_3$](SO$_3$CF$_3$)$_2$ (**6b**) (mp 152 °C). Anal. Calcd for $C_{83}H_{78}S_2F_6O_6P_6Pt_3Te_2$: C, 41.96; H, 3.30; S, 2.69. Found: C, 42.34; H, 3.21; S, 2.41. ^{1}H NMR (CDCl$_3$) δ: 2.94 (br, dppp −CH$_2$), 7.11−7.63 (m, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$) δ: −13.6 [^1J(Pt−P) = 2965 Hz].

(ii) To a benzene solution (10 cm^3) of {C$_5$H$_3$(3-Me)N}$_2$Te$_2$ (48 mg, 0.11 mmol) was added a solution (30 cm^3) of [Pt(dppp)$_2$] (102 mg, 0.10 mmol) in the same solvent with stirring, which continued for 4 h at room temperature. The solvent was evaporated *in vacuo*, and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated dppp. The residue was extracted with benzene, filtered, and passed through a Florisil column to give a yellow powder, [Pt{2-Te-C$_5$H$_3$(3-Me)N}$_2$(dppp)] (**5**) [(yield 44 mg, 42%, mp

Scheme 1



Scheme 2



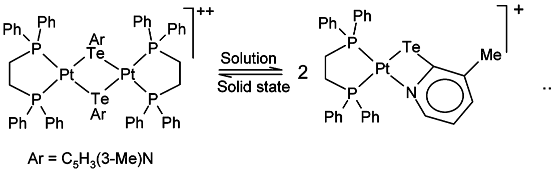
147 °C) Anal. Calcd for $C_{39}H_{38}N_2P_2PtTe_2$: C, 44.74; H, 3.66 N, 2.67. Found: C, 44.73; H, 3.59 N, 2.45. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −10.3 (^1J(Pt−P) = 2740 Hz)], and a benzene-insoluble part, which was extracted with chloroform to afford an orange powder of $[Pt_3Te_2(dppp)_3]Cl_2$ (**6a**) (yield 81 mg, 38%, mp 152 °C). Anal. Calcd for $C_{81}H_{78}Cl_2P_6Pt_3Te_2$: C, 45.28; H, 3.66. Found: C, 44.98; H, 3.43. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −13.6 [^1J(Pt−P) = 2970 Hz].

■ RESULTS AND DISCUSSION

Treatment of $[Pt_2(dppm)_3]$ with $(3\text{-}RC_5H_3N)_2Te_2$ (R = H or Me) in toluene at room temperature gave an oxidative addition product, $[Pt\{2\text{-}TeC_5H_3(3\text{-}R)N\}_2(dppm)]$ (**1**) (R = H (**1a**) and Me (**1b**)), in ~65% yield as a yellow powder together with an orange crystalline product identified as $[Pt\{PPh_2C(TeC_5H_3\text{-}(3\text{-}R)N)_2PPh_2\}_2]$ (**2**) (R = H (**2a**) and Me (**2b**)) in ~20% yield (Scheme 1). The substitution reaction between $[PtCl_2(dppm)]$ and $NaTeC_5H_3(3\text{-}R)N$, prepared *in situ* by reductive cleavage of the Te−Te bond in the corresponding ditellurides by methanolic $NaBH_4$, also gave **1** and **2** (Scheme 2). The ^{31}P NMR spectra of **1** displayed a single resonance at δ ≈ −52 ppm with a $^{195}Pt-^{31}P$ coupling of ~2600 Hz indicative of a tellurolate ligand *trans* to the phosphine ligand.[23−25] The ^{195}Pt NMR spectrum of **1b** exhibited a triplet at δ −4712 ppm with a ^1J(Pt−P) of 2650 Hz due to coupling with two equivalent phosphorus nuclei. The ^{31}P NMR spectra of **2** exhibited signals at −29.3 (**2a**) and −25.1 (**2b**) ppm with a $^{195}Pt-^{31}P$ coupling of ~1900 Hz. The resonance is considerably deshielded with respect to the signal for **1**. The magnitude of ^1J(Pt−P) suggests that the strong *trans*-influencing phosphine ligands are mutually *trans*, which is further confirmed by an X-ray structural analysis of **2a** (see later).

The formation of **2** in these reactions is rather intriguing, as the methylene carbon is attacked by the TeC$_5$H$_3$(3-R)N moiety and is also deprotonated. Deprotonation of the methylene proton in dppm and related ligands R$_2$PCH$_2$L (L = SMe, NHR, PR$_2$, etc.) is well documented in literature.[26] For instance, reactions of [MIr(CO)$_3$(dppm)$_2$] (M = Ir or Rh) with CH$_2$I$_2$ or CH$_2$(I)CN did not yield the expected oxidative addition product; instead products formed by deprotonation of one of the dppm ligands, [MIr(CO)$_2$(μ-I)(μ-CO)(Ph$_2$PCHPPh$_2$)dppm)], are isolated.[27] The reactions of [Pt$_2$(μ-OH)$_2$(dppm)$_2$]$^{2+}$ with LiN(SiMe$_3$)$_2$ in THF deprotonates the dppm ligand rather than the bridging OH to give [Pt$_2$(μ-OH)$_2$(Ph$_2$PCHPPh$_2$)$_2$].[28] Similarly, in amido-bridged complexes, [Pt$_2$(μ-NHR)$_2$(dppm)$_2$]$^{2+}$, deprotonation of dppm by LiN(SiMe$_3$)$_2$ proceeds via the amido group.[29] Double deprotonation of the dppm ligand has also been reported in the literature.[30] For example, reaction of [Ru(CNR)$_2$(dppm)$_2$]$^{2+}$ with [AuCl(PPh$_3$)$_2$] in the presence of KOH affords [Ru(CNR)$_2${PPh$_2$C(AuPPh$_3$)$_2$PPh$_2$}$_2$]$^{2+}$.[30b] In the present study, double deprotonation of the dppm ligand appears to be elicited by strong nucleophilicity of the pyridyltellurolate ligand in both the oxidative addition and substitution reactions. During the oxidative addition reaction, the activated ditellurides by the platinum center attack the dppm ligand to give Ph$_2$PCHTeArPPh$_2$ and ArTeH (Ar = pyridyl group). The former on oxidative addition to platinum (0) may give "Ph$_2$PCTeArPPh$_2$" species. In the case of the substitution reaction, the tellurolate ion attacks the chelating dppm to give "Ph$_2$PCHTeArPPh$_2$PtCl$_2$", which in the presence of base generates "Ph$_2$PCTeArPPh$_2$Pt".

The reaction of [Pt(dppe)$_2$] with (3-RC$_5$H$_3$N)$_2$Te$_2$ gave exclusively an oxidative addition product, [Pt{2-Te-C$_5$H$_3$(3-R)N}$_2$(dppe)] (**3**) (R = H (**3a**), Me (**3b**)), in ~70% yield. Alternatively, **3** could be obtained by the reaction of [PtCl$_2$(dppe)] with two equivalents of NaTeC$_5$H$_3$(3-R)N as described earlier by us.[23] This reaction in the case of 3-methyltellurolate ligand gave a complex of composition Pt{TeC$_5$H$_3$(3-Me)N}(dppe)Cl (**4a**). The latter complex is a nonelectrolyte in chloroform (3.0 μS cm^2 mol^{-1}), while it is a 1:1 elelctrolyte in methanol (83.3 μS cm^2 mol^{-1}) and acetonitrile (70.6 μS cm^2 mol^{-1}). This suggests that the complex exists as a monomeric neutral species with a monodentate tellurolate ligand in chloroform, while in methanol and acetonitrile it adopts an ionic structure with a chelating tellurolate ligand and chloride as counteranion. During the preparation of **4a**, addition of NaBPh$_4$ to the reaction flask resulted in the formation of BPh$_4$ salt [Pt$_2${TeC$_5$H$_3$(3-Me)N}$_2$(dppe)$_2$](BPh$_4$)$_2$ (**4b**). The ^{31}P NMR data of **3b** and **4b** are in agreement with those reported earlier.[23] The magnitude of ^1J(Pt−P) in **3** is consistent with mononuclear *cis* tellurolate complexes.[31,32] It is interesting to note that **4b** is a centrosymmetric dimer stabilized by Te bridges (see later, X-ray crystallography), and the ^{31}P NMR spectrum showed two signals with different ^1J(Pt−P) values. A similar ^{31}P NMR pattern has been reported for [Pt$_2$(μ-SeCH$_2$CH$_2$NMe$_2$)$_2$(dppe)$_2$]$^{2+}$.[33] Initially, in the absence of X-ray structural analysis,[23,33] asymmetric Pt−E (E = Se or Te) bridges have been suggested for these complexes. It is likely that, in solution, a monomeric species containing a chelating tellurolate ligand may form (eq 1). The strong *trans* influence of the phosphine ligand may weaken the Pt−Te−Pt bridge. Such a mononuclear species would show two ^{31}P NMR resonances with different ^1J(Pt−P) coupling constants, one due to a Ph$_2$P group *trans* to nitrogen (^1J(Pt−P) = 3267 Hz) and another for that *trans* to the tellurolate ligand (^1J(Pt−P) = 2940 Hz).



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The reaction of [Pt(dppp)$_2$] with (3-RC$_5$H$_3$N)$_2$Te$_2$ in benzene, in addition to oxidative addition product [Pt{2-Te-C$_5$H$_3$(3-Me)-N}$_2$(dppe)] (**5**), gave an ionic trinuclear complex, [Pt$_3$Te$_2$-(dppp)$_3$]Cl$_2$ (**6a**). Similarly, a substitution reaction of [PtCl$_2$-(dppp)] with NaTeC$_5$H$_3$(3-Me)N gave a mixture of **5** and **6a**, which were separated by column chromatography. Treatment of **6a** with AgOTf gave the corresponding OTf complex [Pt$_3$Te$_2$-(dppp)$_3$][OTf]$_2$ (**6b**). Formation of similar tellurido-bridged

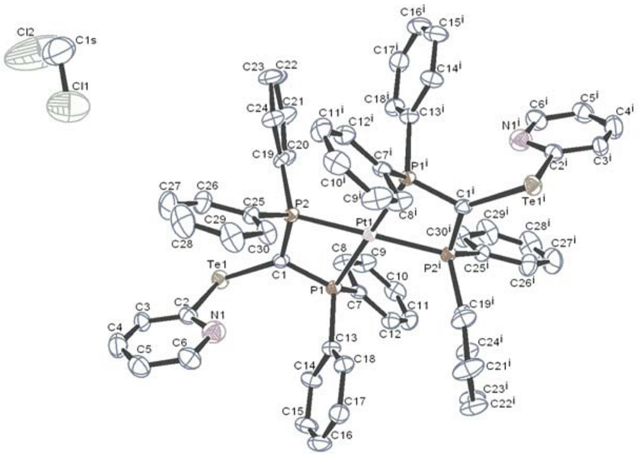

Figure 1. Crystal structure of [Pt{PPh$_2$C(TeC$_5$H$_4$N)$_2$PPh$_2$}$_2$]·2CH$_2$Cl$_2$ (**2a**·2CH$_2$Cl$_2$) with atomic numbering scheme. The ellipsoids are drawn at 50% probability.

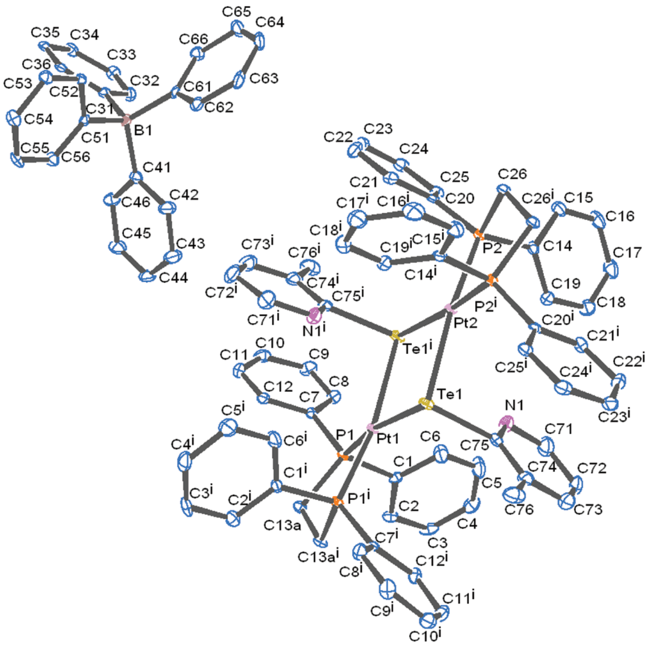

Figure 2. Crystal structure of [Pt$_2${TeC$_5$H$_3$(3-Me)N}$_2$(dppe)$_2$]·(BPh$_4$)$_2$ (**4b**) with atomic numbering scheme. The ellipsoids are drawn at 50% probability.

trinuclear platinum complex $[Pt_3(\mu\text{-}Te)_2(Th)(PPh_3)_5]Cl$ has been reported by oxidative addition reaction of Th_2Te_2 to $[Pt(PPh_3)_4]$ in dichloromethane.[14]

The ^{31}P NMR spectrum of **5** exhibited a singlet at δ −10.3 ppm with a $^{1}J(Pt{-}P)$ of 2744 Hz, while the spectrum of **6b** showed a resonance at lower frequency (δ −13.6 ppm) with a $^{1}J(Pt{-}P)$ of 2965 Hz. The NMR data are consistent with the reported values.[34] The chemical structure of **6b** was confirmed by X-ray structural analysis. There are two independent tellurido-bridged (Pt−Te = 2.62 Å (av); Pt−Te bond distance in $[Pt_3(\mu\text{-}Te)_2(PEt_3)_6]^{2+}$[35] and $[Pt_3(\mu\text{-}Te)_2(Th)(PPh_3)_5]Cl$[14] is 2.604 and 2.630 Å, respectively) cations in the crystal; one molecule has a 2-fold symmetry, while the other has a 3-fold symmetry. However, due to disorder in the OTF counterions, the structure is not described here (Supporting Information).

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $[Pt\{PPh_2C(TeC_5H_4N)_2PPh_2]\cdot 2CH_2Cl_2$ (2a·2CH₂Cl₂)

Pt1−P1	2.3292(17)	Te1−C2	2.144(8)
Pt1−P2	2.3116(18)	P1−C1	1.742(8)
Te1−C1	2.059(7)	P2−C1	1.750(7)
P2−Pt1−P2′	180.00(9)	C19−P2−Pt1	115.8(2)
P2−Pt1−P1′	109.34(6)	P1−C1−P2	100.5(4)
P2−Pt1−P1	70.66(6)	P1−C1−Te1	131.1(4)
C1−Te1−C2	99.3(3)	P2−C1−Te1	127.6(4)
C1−P2−Pt1	94.6(3)	N1−C2−Te1	121.9(7)
C25−P2−Pt1	117.8(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) of $[Pt_2\{TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2]\cdot[BPh_4]_2$ (4b)

Pt(1)−P(1)	2.2555(11)	Pt(2)−P(2)	2.2523(11)
Pt(1)−Te(1)	2.6382(4)	Pt(2)−Te(1)	2.6318(4)
Pt(1)−Te(1)#1	2.6383(4)	Te(1)−C(75)	2.168(5)
P(1)−Pt(1)−Te(1)	168.98(3)	P(2)−Pt(2)−Te(1)	173.36(3)
P(1)−Pt(1)−Te(1)#1	95.87(3)	Te(1)#1−Pt(2)−Te(1)	85.064(19)
Te(1)−Pt(1)−Te(1)#1	84.806(19)	C(75)−Te(1)−Pt(2)	94.09(12)
P(2)#1−Pt(2)−P(2)	85.72(6)	C(75)−Te(1)−Pt(1)	90.65(12)
P(2)#1−Pt(2)−Te(1)#1	173.36(3)	Pt(2)−Te(1)−Pt(1)	95.066(16)
P(2)−Pt(2)−Te(1)#1	94.99(3)	N(1)−C(75)−Te(1)	114.6(3)
P(2)#1−Pt(2)−Te(1)	95.00(3)		

X-ray Crystallography. The molecular structures of $[Pt\{Ph_2PC(TeC_5H_4N)PPh_3\}_2]$ (**2a**) and $[Pt_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2][BPh_4]_2$ (**4b**), established by X-ray diffraction analysis, are shown in Figures 1 and 2. Selected interatomic parameters are summarized in Tables 2 and 3. The platinum atom in **2a** adopts a distorted square-planar configuration defined by a "P_4" coordination core. The chelate P1−Pt1−P2 angle is acute (70.66°); as a consequence, the adjacent angles are opened up. The Pt−P distances are similar (2.31−2.33 Å) and are slightly longer than those reported for $[PtSe_4(dppe)]$ (2.24 Å),[36] $[Pt_3(\mu\text{-}Stol)_4(dppm)_2][CF_3SO_3]_2$ (2.25 Å),[24] and $[Pt\{o\text{-}C_6H_4(PPh_2)_2\}(PhC{\equiv}CPh)]$ (2.26 Å).[37] The Te−C distances are as expected.[23,38] Various angles involving the C-1 carbon vary between 100.5° and 131.1°, indicative of a trigonal (allylic-type) configuration.

Compound **4b** is a centrosymmetric dimer comprised of two distorted square-planar platinum atoms that are held together by tellurolato bridges. Coordination around each platinum is defined by a P_2Te_2 donor set from a chelating dppe ligand and two tellurolate ligands. The Pt−P and Pt−Te distances are as expected.[2,15,17] The four-membered Pt_2Te_2 ring is planar with $C_5H_3(3\text{-}Me)N$ groups adopting an *anti* configuration.

Theoretical Calculations. The bonding, charge transfer, and geometry of compounds $[Pt\{2\text{-}Te\text{-}C_5H_3(3\text{-}R)N\}_2(dppm)]$ (**1**), $[Pt\{PPh_2C(TeC_5H_3(3\text{-}R)N)_2PPh_2\}_2]$ (**2**), and $[Pt_3Te_2(dppp)_3]^{2+}$ (**6**) have been analyzed through relativistic density functional calculations.[39] The formation of products **1** and **2** shows a clear preference for **1**. These systems differ by the substitution of the dppm ligand with a $(3\text{-}RC_5H_3N)Te$ moiety, which leads to changes in the ligand-to-metal charge transfer. In order to characterize the latter point, we performed a detailed charge analysis employing the Hirshfeld partitioning schemes of the electron density, focusing on the charge distribution between the dppm and $\{PPh_2C(TeC_5H_3(3\text{-}R)N)_2PPh_2\}$ ligands in systems **1** and **2**, respectively. The calculations characterize a more efficient charge donation toward the Pt center for **1** (0.37 e), in comparison to **2**, which shows an almost negligible donation (0.08 e). These results suggest that a stronger bond is formed between Pt and dppm ligand in compound **1**, accounting for the described preference (see text).

The formation of system **6**, which exhibits a $[Pt_3(dppp)_3]^{6+}$ core stabilized by a $[Te_2]^{4-}$ fragment as ligand, participates in the making of the Pt−Te bond that results from the direct 5d-Pt−5p-Te interaction. The molecular orbital diagram in Figure 3

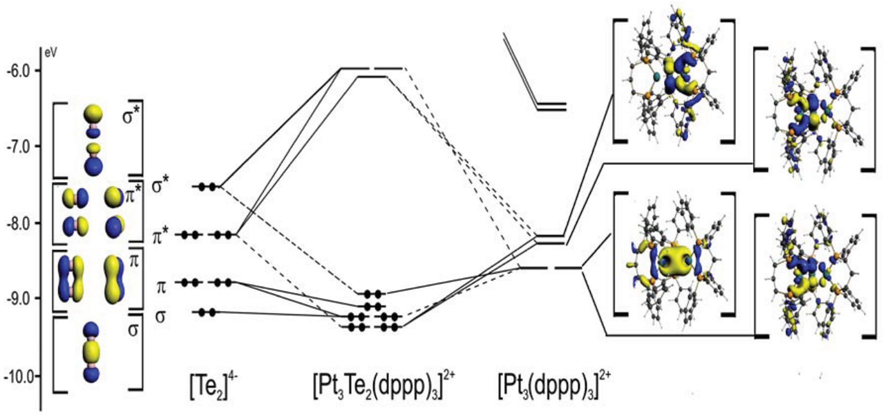

Figure 3. Molecular orbital diagram describing the core fragment interaction and $[Te_2]^{4-}$ in compound **6**.

denotes the contribution from the $[Te_2]^{4-}$ toward the electronic structure of $[Pt_3Te_2(dppp)_3]^{2+}$, which arises mainly from the σ, π, π^*, and σ^* 5p-Te combinations. The HOMO (Figure 4) is formed mainly by a 5d−5p bonding interaction between the Pt_3 and the σ^* combination of Te_2, while the LUMO shows an antibonding interaction involving a π^*combination of Te_2. The charge donation from the Te_2 moiety toward the core gives an overall charge transfer of about 1.73 e, leading to $[Te_2]^{2.27-}$ and $[Pt_3(dppp)_3]^{4.27+}$ fragments.

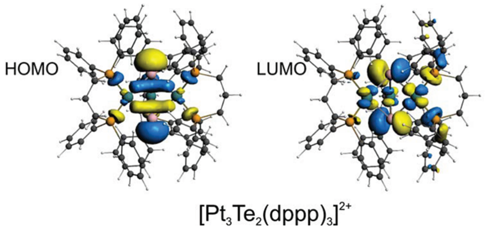

Figure 4. Isosurface of the HOMO and LUMO of compound **6**.

CONCLUSION

The oxidative addition reactions of (diphosphine)Pt^0 with dipyridyl ditellurides and substitution reactions of $[PtCl_2(P^\frown P)]$ ($P^\frown P$ = dppm, dppe, dppp) with 2-pyridyltellurolate ions not only afforded expected products but also gave serendipitous derivatives. Quite often a mixture of products were formed that could be separated by recrystallization or column chromatography. The nature of the isolable products depended on chelating phosphine and the substituent in the pyridyl ring. The bonding, charge transfer, and geometry of compounds $[Pt\{2\text{-}Te\text{-}C_5H_3(3\text{-}R)N\}_2(dppm)]$ (**1**), $[Pt\{PPh_2C(TeC_5H_3(3\text{-}R)N)_2\text{-}PPh_2\}_2]$ (**2**), and $[Pt_3Te_2(dppp)_3]^{2+}$ (**6**) have been analyzed through relativistic density functional calculations.

ASSOCIATED CONTENT

Supporting Information

CCDC-Nos. 851583 and 851585 for $[Pt\{PPh_2C(TeC_5H_4N)_2\text{-}PPh_2\}_2]\cdot 2CH_2Cl_2$ (**2a**$\cdot 2CH_2Cl_2$) and $[Pt_2\{\mu\text{-}TeC_5H_3(3\text{-}Me)N\}_2(dppe)_2]\cdot[BPh_4]_2$ (**4b**), respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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