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Aryltellurenyl Cation $[RTe(CR'_2)]^+$ Stabilized by an N-Heterocyclic Carbene

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The reaction of the (mixed-valent) aryltellurenyl halides $RTeTeCl_2R$ (**1**), $RTeTeBr_2R$ (**2**) and RTeI (**3**, R = 2,6-$Mes_2C_6H_3$) with 1,3,4,5-tetramethylimidazol-2-ylidene (CR'_2) provides cationic aryltellurenyl carbene complexes of the type $[RTe(CR'_2)]^+ A^-$ (**4**, A = $RTeCl_2$; **5**, A = $RTeBr_2$; **6**, A = I). The stabilization energy and natural charge distribution of the model cation $[PhTe(CR'_2)]^+$ as well as the related σ-donor-stabilized cations $[PhTe(PMe_3)]^+$, $[I(CR'_2)]^+$, $[I(PMe_3)]^+$ were investigated by DFT calculations and NBO analyses.

Introduction

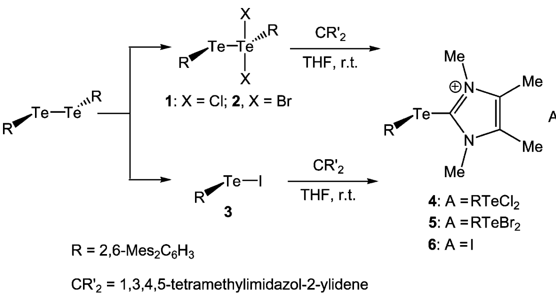
The aryltellurenyl "RTe" moiety possesses substantial pseudohalogen character and is often interchangeable with iodine. For instance, the diaryl ditelluride RTeTeR (e.g., R = 2,4,6-$tBu_3C_6H_2$[1]) and the series of aryltellurenyl halides RTeX (X = I,[2,3] Br,[2,4] Cl[5]) closely resemble molecular iodine I_2 or the related interhalides IBr and ICl, while $RTeCl_3$[5] can be regarded as being an analogue of ICl_3. The tritelluride anions $(RTe)_3^-$ (e.g., R = Ph,[6] CF_3[7]) and the related diiodotelluride anion $(RTeI_2)^-$ (e.g., R = CF_3[7]) exhibit characteristics very similar to the triiodide ion I_3^-.

It is well known that iodine readily forms σ-donor-stabilized cations $[I(L_n)]^+$, such as $[I(pyr)_2]^+$,[8] which have recently found a variety of applications in organic synthesis.[9] Despite the evident pseudohalogen character, organotellurenyl cations $[RTe(L_n)]^+$ are extremely rare. The aryltellurenyl cation $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Te]^+ PF_6^-$ containing an intramolecularly coordinating ligand has been communicated, however, no structural details were disclosed.[10] The fully characterized di- and trinuclear tellurium species $[MesTe(TeMes_2)_n]^+ SbF_6^-$ (n = 1, 2) are regarded as complexes between the mesityltellurenyl cation $MesTe^+$ and the Lewis base Mes_2Te.[11] However, $[MesTe(TeMes_2)]^+ SbF_6^-$ contains rather short cation–anion contacts [Te···F 2.768(3) Å]. Two phosphane-stabilized organotellurenyl cations, $[4\text{-}FC_6H_4Te(PBu_3)]^+ BF_4^-$ and $[MeTe(PBu_3)]^+ ClO_4^-$, have been described briefly as oils and could be characterized only tentatively by ^{31}P- and ^{125}Te-NMR spectroscopy.[12]

Recently, we have communicated that chlorination and bromination of the diaryl ditelluride RTeTeR (R = 2,6-$Mes_2C_6H_3$) affords the mixed-valent aryltellurenyl halides $RTeTeX_2R$ (**1**, X = Cl; **2**, X = Br; R = 2,6-$Mes_2C_6H_3$), whereas iodination gives rise to the expected aryltellurenyl iodide 2,6-$Mes_2C_6H_3TeI$ (**3**).[13] We now report on the reactivity of **1**–**3** towards a strong σ-donor, namely an N-heterocyclic carbene CR'_2. These reactions provide access to a new series of cationic aryltellurenyl carbene complexes $[RTe(CR'_2)]^+ A^-$ (**4**, A = $RTeCl_2$; **5**, A = $RTeBr_2$; **6**, A = I; CR'_2 = 1,3,4,5-tetramethylimidazol-2-ylidene). The reaction type is similar to that observed for the tetranuclear phenyltellurenyl iodide $(PhTeI)_4$ and Ph_3P, the reaction of which leads to the complex $PhTe(PPh_3)I$, which, however, contains rather covalent Te–I bonds [3.0930(9) Å].[14]

Results and Discussion

In the presence of an N-heterocyclic carbene (CR'_2, 1,3,4,5-tetramethylimidazol-2-ylidene) the mixed-valent aryltellurenyl halides $RTeTeX_2R$ (**1**, X = Cl; **2**, X = Br; R = 2,6-$Mes_2C_6H_3$) readily undergo heterolytic Te–Te bond cleavage to form the σ-donor-stabilized aryltellurenyl cation $[2,6\text{-}Mes_2C_6H_3Te(CR'_2)]^+ (2,6\text{-}Mes_2C_6H_3TeX_2)^-$ (**4**, X = Cl; **5**, X = Br) in yields of 84 and 91 % (Scheme 1). Under similar conditions, the reaction of the monomeric aryltellurenyl iodide 2,6-$Mes_2C_6H_3TeI$ (**3**) with the same N-heterocyclic carbene CR'_2 gives rise to the formation of the σ-donor-



Scheme 1.

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stabilized aryltellurenyl cation [2,6-$Mes_2C_6H_3Te(CR'_2)]^+$ I^- (**6**) in 91% yield.

In the light of the analogy between the aryltellurenyl "RTe" moiety and iodine, the [2,6-$Mes_2C_6H_3Te(CR'_2)]^+$ cation of **4**–**6** is comparable with the carbene iodine adduct $[I(CR''_2)]^+$ I^- (CR''_2, 1,3-diethyl-4,5-dimethylimidazol-2-ylidene),[15] whereas the (2,6-$Mes_2C_6H_3TeX_2)^-$ (X = Cl, Br) anions of **4** and **6** can be regarded as being analogues of $(ICl_2)^-$ and $(IBr_2)^-$. The X-ray structures of **4** and **6** are shown in Figures 1 and 2. Selected bond parameters are collected in the caption of the Figures. The cations and anions are associated via secondary Te···Cl [3.270(4) Å] and Te···I [3.651(6) Å] contacts that are shorter than the sum of the van der Waals radii (Te/Cl 3.81 Å, Te/I 4.04 Å). The Te–C_{Carb} bond lengths of **4** [2.091(8) Å] and **6** [2.097(2) Å] are somewhat shorter than the Te–C_{Ar} bond length of the cation of **4** [2.146(7) Å] and **6** [2.161(2) Å] and the anion of **4** [2.141(7) Å], but compare well with the I–C_{Carb} bond length of $[I(CR''_2)]^+$ I^- [2.104(3) Å].[15] The C–Te–C angle of the cation is nearly rectangular. The [2,6-$Mes_2C_6H_3TeCl_2]^-$ anion of **4** reveals Te–Cl bonds [av. 2.623(2) Å] that are somewhat longer than those of the parent compound $RTeTeCl_2R$ [**1**, av. 2.517(5) Å] and $(Ph_4P)^+$ ICl_2^- [2.571(2) Å].[16] The Cl–Te–Cl angle of **4** is almost linear. The solid structures of **4**–**6** are retained in CD_2Cl_2 solution. The ^{13}C-NMR spectra of **4** and **5** show two sets of signals for the *m*-terphenyl substituent. The carbene carbon atoms of **4**–**6** gives rise to a signal at δ 128.9, which is substantially shifted downfield with respect to $[I(CR''_2)]^+$ I^- [δ(^{13}C) 109.4].[15] No evidence was found for ^{125}Te satellites. The [2,6-$Mes_2C_6H_3Te(CR'_2)]^+$ cation of **4**–**6** reveals a ^{125}Te NMR resonance at δ = 444.7, whereas no signal was found for the (2,6-$Mes_2C_6H_3TeX_2)^-$ anions of **4** (X = Cl) and **5** (X = Br), which is tentatively explained by a dynamic process compromising the constitutional stability in solution. The ESI MS spectra (positive mode, MeCN) of **4**–**6** exhibit only one prominent mass cluster at 567.20 g mol^{-1}, which was unambiguously assigned to the [2,6-$Mes_2C_6H_3$-$Te(CR'_2)]^+$ cation (CR'_2, 1,3,4,5-tetramethylimidazol-2-ylidene).

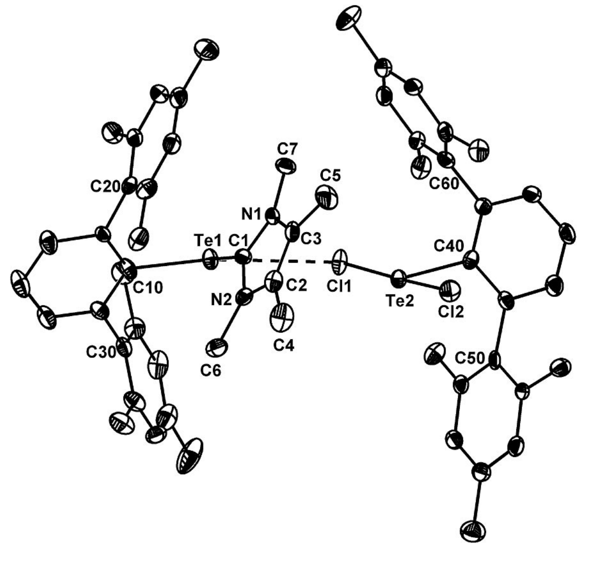

Figure 1. Molecular structure of **4** showing 30% probability ellipsoids and the crystallographic numbering scheme (the second crystallographically independent albeit similar conformer is not shown). Selected bond parameters [Å, °]: Te1–C1 2.091(8), Te1–C10 2.146(7), Te2–Cl1 2.615(2), Te2–Cl2 2.631(2), Te2–C40 2.141(7), N1–C1 1.354(9), N1–C3 1.405(10), N1–C7 1.462(9), N2–C1 1.353(9), N2–C2 1.380(9), N2–C6 1.456(9), Te1···Cl1 3.270(4), C1–Te1–C10 97.7(3), C40–Te2–Cl1 92.30(19), C40–Te2–Cl2 92.32(19), Cl1–Te2–Cl2 173.99(6), N1–C1–Te1 126.6(6), N1–C1–N2 106.3(7), N2–C1–Te1 126.8(5), C1–N1–C3 109.7(6), C1–N1–C7 125.2(7), C1–N2–C2 109.8(6), C1–N2–C6 125.3(6), C2–N2–C6 124.9(7).

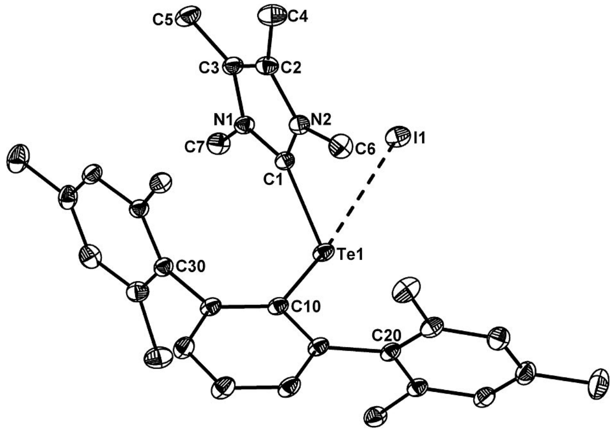

Figure 2. Molecular structure of **6** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1–C1 2.097(2), Te1–C10 2.161(2), N1–C1 1.342(3), N1–C3 1.378(3), N1–C7 1.464(3), N2–C1 1.347(3), N2–C2 1.385(3), N2–C6 1.460(3), C3–C2 1.358(3), Te1···I1 3.651(6), C1–Te1–C10 97.20(8), N1–C1–N2 106.89(18), C1–N1–C3 109.83(18), C1–N1–C7 125.68(19), C3–N1–C7 124.42(18), C1–N2–C2 109.55(18), C1–N2–C6 125.09(19), C2–N2–C6 125.3(2).

DFT Calculations and NBO Analyses

In an effort to compare carbene and phosphane coordinated phenyltellurenyl and iodonium cations isolated in the gas phase, the geometry of the model complexes $[PhTe(CR'_2)]^+$, $[PhTe(PMe_3)]^+$, $[I(CR'_2)]^+$ and $[I(PMe_3)]^+$ (CR'_2 = 1,3,4,5-tetramethylimidazol-2-ylidene) was optimized at the DFT/B3PW91 level of theory. The minimum energy structures, selected bond parameters and dissociation energies E_{Diss} are shown in Figure 3. Consistent with the general observation that carbenes are better σ-donors than phosphanes, the carbene complexes $[PhTe(CR'_2)]^+$ (424.1 KJ mol^{-1}) and $[I(CR'_2)]^+$ (796.4 kJ mol^{-1}) possess higher dissociation energies E_{Diss} than their phosphane counterparts $[PhTe(PMe_3)]^+$ (328.6 kJ mol^{-1}) and $[I(PMe_3)]^+$ (709.8 kJ mol^{-1}). The dissociation energies E_{Diss} of the iodonium cations are approximately twice the value of the phenyltellurenyl cations, which suggests that a significant amount of the positive charge in the bare phenyltellurenyl cations is delocalized over the phenyl ring. The spatial arrangement around the Te atom in $[PhTe(CR'_2)]^+$ closely resembles that of the [2,6-$Mes_2C_6H_3Te(CR'_2)]^+$ cation of

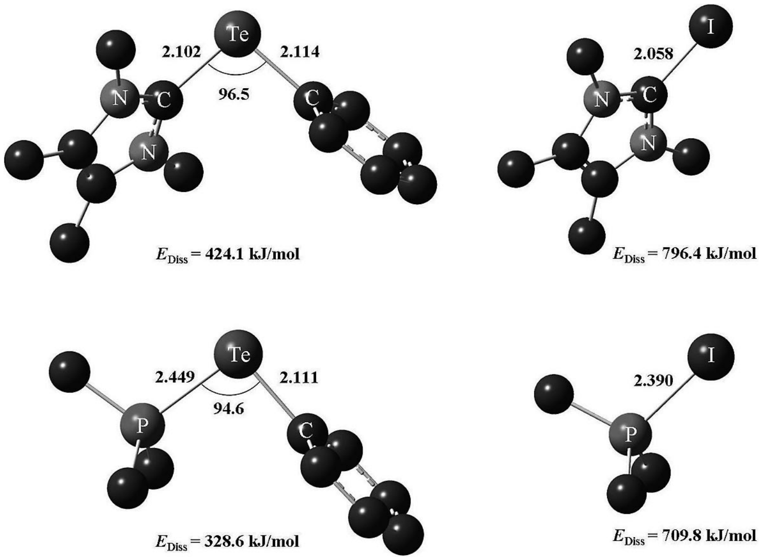

Figure 3. Geometry-optimized structures, selected bond parameters [Å, °] and dissociation energies E_{Diss} of the model σ-donor complexes $[PhTe(CR'_2)]^+$, $[PhTe(PMe_3)]^+$, $[I(CR'_2)]^+$ and $[I(PMe_3)]^+$ (CR'_2, 1,3,4,5-tetramethylimidazol-2-ylidene).

4 and **6** (CR'_2, 1,3,4,5-tetramethylimidazol-2-ylidene) and related bond parameters are virtually identical. The donor acceptor distance increases in the order $[I(CR'_2)]^+$ (2.058 Å) > $[PhTe(CR'_2)]^+$ (2.102 Å) >> $[I(PMe_3)]^+$ (2.390 Å) > $[PhTe(PMe_3)]^+$ (2.449 Å).

For the same model complexes NBO analyses were carried out and the natural charge distribution as well as the transfer of natural charge upon complex formation collected in Table 1. The Te atom of $[PhTe(CR'_2)]^+$ can accommodate the highest natural charge (0.711) of all model cations. In the same complex the positive charge is almost evenly distributed between the aryltellurenyl cation $PhTe^+$ (0.489) and the carbene moiety (0.511). For the other three model complexes more than half of the positive charge is located at the σ-donor, which is most pronounced within $[I(PMe_3)]^+$ (0.865). The increase of natural charge upon complex formation affects all atoms within the σ-donors including the methyl substitutents. In the phosphane complexes more natural charge is transferred from the cation to the σ-donor than in the carbene complexes. Comparing separately the carbene complexes $[PhTe(CR'_2)]^+$ and $[I(CR'_2)]^+$ as well as the phosphane complexes $[PhTe(PMe_3)]^+$ and $[I(PMe_3)]^+$, more natural charge is transferred upon complex formation to the iodonium cation than to the phenyltellurenyl cation.

Experimental Section

General: The (mixed valent) aryltellurenyl halides **1**–**3** and the 1,3,4,5-tetramethylimidazol-2-ylidenes (CR'_2) were prepared according to known routes.[13,17] NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and are referenced against Me_4Si and Me_2Te. IR spectra were recorded with a 5 SXC Nicolet DTGS FT-IR spectrometer. The electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK). Microanalyses were obtained by means of a Vario EL elemental analyzer.

Table 1. Selected natural charges and the transfer of natural charges upon complex formation (in brackets) of $[PhTe(CR'_2)]^+$, $[PhTe(PMe_3)]^+$, $[I(CR'_2)]^+$ and $[I(PMe_3)]^+$ (CR'_2, 1,3,4,5-tetramethylimidazol-2-ylidene).

	$[PhTe(CR'_2)]^+$	$[PhTe(PMe_3)]^+$	$[I(CR'_2)]^+$	$[I(PMe_3)]^+$
p-CH	0.053 (–0.182)	0.065 (–0.170)		
m-CH[a]	0.038 (–0.007)	0.043 (–0.002)		
o-CH[a]	0.005 (–0.130)	0.010 (–0.125)		
i-C	–0.362 (0.098)	–0.379 (0.081)		
Te	0.711 (–0.154)	0.514 (–0.352)		
I			0.378 (–0.622)	0.135 (–0.865)
C_{Carb}	0.129 (0.045)		0.214 (0.130)	
N-Me	–0.376 (0.072)		–0.384 (0.064)	
N-*Me*	0.309 (0.058)		0.319 (0.068)	
C-Me	0.169 (0.049)		0.174 (0.053)	
C-*Me*	0.089 (0.054)		0.096 (0.061)	
P-Me		1.092 (0.356)		1.213 (0.477)
P-*Me*		–0.133 (0.113)		–0.116 (0.129)
Σ cation	0.489 (–0.511)	0.306 (–0.694)	0.378 (–0.622)	0.135 (–0.865)
Σ σ-donor	0.511 (0.511)	0.694 (0.694)	0.622 (0.622)	0.865 (0.865)

[a] average values.

Synthesis of 2-(2′,6′-Dimesitylphenyltellurenyl)-1,3,4,5-tetramethylimidazolium 2,6-Dimesitylphenyldichlorotellurate (4): A solution of **1** (760 mg, 0.80 mmol) in THF (50 mL) was treated with a 0.2 M THF solution of 1,3,4,5-tetramethylimidazol-2-ylidene (4.0 mL, 0.80 mmol). The colour changed immediately from blue to orange. The solvent was removed in vacuo and the crude product recrystallized from CH_2Cl_2/hexane. Yield 711 mg (0.66 mmol; 83%, m.p. 202–203 °C) of orange crystals. ^1H NMR (CD_2Cl_2): δ = 7.41 (t, J = 8 Hz, 2 H, Ar-H), 7.03 (d, J = 8 Hz, 4 H, Ar-H), 6.88 (s, 4 H, Ar-H), 6.83 (s, 4 H, Ar-H), 3.28 (s, 6 H, Carb-H4), 2.32 (s, 12 H, Me), 2.06 (s, 6 H, Carb-H3), 2.03 (s, 12 H, Me), 2.00 (s, 12 H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ = 151.2, 145.8, 143.5, 138.8, 137.7, 136.8, 135.6, 135.3, 129.7, 129.2, 128.7, 127.4, 127.3, 126.9 (Ar-C), 128.9 (Carb-C1), 124.2, 123.3 (Ar-C), 116.6 (Carb-C2), 37.9 (Carb-C4), 21.7, 20.2, 21.1, 20.9 (Me), 9.6 (Carb-C3) ppm. ^{125}Te NMR (CD_2Cl_2): δ = 444.7 . ESI MS (positive mode, 150 V, MeCN): m/z = 567.20 [correct mass and isotopic pattern for $RTe(C_5H_8N_2)^+$]. $C_{55}H_{62}Cl_2N_2Te_2$ (1077.28): C 61.32, H 5.80; found C 61.52, H 5.91.

Synthesis of 2-(2′,6′-Dimesitylphenyltellurenyl)-1,3,4,5-tetramethylimidazolium 2,6-Dimesitylphenyldibromotellurate (5): A solution of **2** (833 mg, 0.80 mmol) in THF (50 mL) was treated with a 0.2 M THF solution of 1,3,4,5-tetramethylimidazol-2-ylidene (4.0 mL, 0.80 mmol). The colour changed immediately form blue to orange. The solvent was removed in vacuo and the crude product recrystallized from CH_2Cl_2/hexane. Yield 853 mg (0.73 mmol; 91%, m.p. 224–225 °C) of orange crystals. ^1H NMR (CD_2Cl_2): δ = 7.39 (t, J = 8 Hz, 2 H, Ar-H), 7.09 (d, J = 8 Hz, 4 H, Ar-H), 6.99 (s, 4 H, Ar-H), 6.86 (s, 4 H, Ar-H), 3.33 (s, 6 H, Carb-H4), 2.30 (s, 12 H, Me), 2.09 (s, 18 H, Carb-H3), 2.00 (s, 12 H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ = 150.1, 145.6, 138.5, 137.5, 136.6, 136.4, 135.1, 130.6, 129.5, 129.2, 128.7, 127.8, 127.6, 126.9 (Ar-C), 128.9 (Carb-C1), 126.8, 124.8 (Ar-C), 116.6 (Carb-C2), 37.9 (Carb-C4), 21.6, 20.3, 21.0, 20.9 (Me), 9.6 (Carb-C3) ppm. ^{125}Te NMR (CD_2Cl_2): δ = 444.7 ppm. ESI MS (positive mode, 150 V, MeCN): m/z = 567.20 [correct mass and isotopic pattern for $RTe(C_5H_8N_2)^+$]. $C_{55}H_{62}Br_2N_2Te_2$ (1166.19): C 56.65, H 5.36; found C 56.52, H 5.47.

Synthesis of 2-(2′,6′-Dimesitylphenyltellurenyl)-1,2,4,5-tetramethylimidazolium Iodide (6): A solution of **3** (910 mg, 1.60 mmol; R = 2,6-$Mes_2C_6H_3$) in THF (50 mL) was treated with a 0.2 M THF solution of 1,3,4,5-tetramethylimidazol-2-ylidene (4.0 mL, 0.80 mmol). The colour changed immediately from green to colourless. The solvent was removed in vacuo and the crude product recrystallized from CH_2Cl_2/hexane. Yield 1.40 g (1.46 mmol; 91%, m.p. 256–257 °C) of colourless crystals. ^1H NMR (CD_2Cl_2): δ = 7.39 (t, J = 8 Hz, 1 H, Ar-H), 6.99 (d, J = 8 Hz, 2 H, Ar-H), 6.86 (s, 4 H, Ar-H), 3.49 (s, 6 H, Carb-H4), 2.33 (s, 6 H, Me), 2.15 (s, 6 H, Carb-H3), 2.01 (s, 12 H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ = 145.4, 138.4, 137.5, 135.1, 129.5, 129.1 (Ar-C), 128.9 (Carb-C1), 128.6 (Ar-C), 116.9 (Carb-C2), 111.4 (Ar-C), 38.5 (Carb-C4), 21.0 (Me), 20.2 (Me), 10.0 (Carb-C3) ppm. ^{125}Te NMR (CD_2Cl_2): δ = 444.7 ppm. ESI MS (positive mode, 150 V, MeCN): m/z = 567.20 [correct mass and isotopic pattern for $RTe(C_5H_8N_2)^+$]. $C_{31}H_{37}IN_2Te$ (692.18): C 53.79, H 5.39; found C 53.51, H 5.29.

Crystallography: Single crystals suitable for X-ray crystallography were grown from toluene (for **4**) and benzene (for **6**). Intensity data were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-K_α (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS.[18] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[19] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Crystal and refinement data are collected in Table 2. Figures were created using DIAMOND.[20]

Table 2. Crystal data and structure refinement of **4** and **6**.

	4·toluene	**6**
Formula	$C_{55}H_{62}Cl_2N_2Te_2 \cdot C_7H_8$	$C_{31}H_{37}IN_2Te$
Formula weight [g mol^{-1}]	1169.30	692.13
Crystal system	monoclinic	monoclinic
Crystal size [mm]	0.39 × 0.16 × 0.08	0.58 × 0.18 × 0.1
Space group	$P2_1/n$	$P2_1/n$
a [Å]	28.860(5)	9.0453(14)
b [Å]	13.253(2)	15.059(2)
c [Å]	29.378(5)	21.610(3)
α [°]	90	90
β [°]	93.616(4)	90.631(4)
γ [°]	90	90
V [Å^3]	11214(3)	2943.4(8)
Z	8	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.385	1.562
T [K]	173	173
μ(Mo-K_a) [mm^{-1}]	1.175	2.080
F(000)	4752	1368
θ range [°]	0.99 to 25.02	1.88 to 30.52
Index ranges	$-34 \leq h \leq 22$	$-12 \leq h \leq 12$
	$-15 \leq k \leq 15$	$-21 \leq k \leq 21$
	$-34 \leq l \leq 30$	$-29 \leq l \leq 30$
No. of reflections collected	61149	36017
Completeness to θ_{max}	99.9%	98.8%
No. of independent reflections	19797	8883
No. of obsd. reflections with [$I > 2\sigma(I)$]	10142	7674
No. of refined parameters	1225	316
GooF (F^2)	0.949	1.044
R_1 (F) [$I > 2\sigma(I)$]	0.0563	0.0262
wR_2 (F^2) (all data)	0.1612	0.0740
$(\Delta/\sigma)_{max}$	0.002	> 0.000
Largest diff. peak/hole [e·Å^{-3}]	1.477/–0.643	0.986/–0.531

CCDC-675257 (for **4**) and -675258 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methodology: All calculations were carried out using the Gaussian 03 suite of programs.[21] The geometries were fully optimized at the DFT/B3PW91[22] level of theory using the large-core correlation-consistent SDB-cc-pVTZ basis sets with the appropriate relativistic electron core potential[23] for the heavy atoms Te and I and the split-valence 6-311+G(d,p) basis set for atoms C, N, P and H. Frequency calculations have been carried out to confirm that all the stationary points are minima on the potential energy surface (PES). The dissociation energies E_{Diss} have been obtained from the difference of the molecular energies of the complexes and the corresponding isolated molecules. They have been corrected for zero-point vibrational energies and for basis set superposition errors using the counterpoise procedure.[24] The BSSE energies are 3.75 kJ mol^{-1} for $[PhTe(CR_2)]^+$, 5.69 kJ mol^{-1} for $[PhTe(PMe_3)]^+$, 13.23 kJ mol^{-1} for $[I(CR'_2)]^+$ and 13.38 kJ mol^{-1} for $[I(PMe_3)]^+$. Analyses of the natural charges and the transfer of natural charge upon complex formation have been performed using Weinhold's natural bond orbital (NBO) theory[25] and the NBO 3.1[26] program as implemented in Gaussian 03.

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