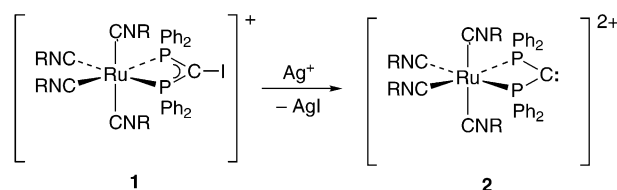


silver(I) salts (AgClO_4 or AgBF_4) (Scheme 1), a nonstandard method of carbene generation. Thus the formally anionic diphosphanyliodomethanide ligand $\{(\text{PPh}_2)_2\text{CI}\}^-$ is converted into the neutral ligand $(\text{PPh}_2)_2\text{C}$. Coordination of the diphosphanylcarbene $(\text{PPh}_2)_2\text{C}$ to the metal fragment



Scheme 1. Formation of the transient metalladiphosphanylcarbene **2**. $\text{R} = \text{tBu}$.

Carbene Chemistry

Trapping Highly Electrophilic Metalladiphosphanylcarbenes**

Javier Ruiz,* Marta E. G. Mosquera, Gabriel García, Elena Patrón, Víctor Riera, Santiago García-Granda, and Francisco Van der Maelen

In recent years much attention has been paid to the study of nucleophilic carbenes of Arduengo type (N-heterocyclic carbenes)^[1] and related diaminocarbenes $(\text{R}_2\text{N})_2\text{C}$,^[2] which are stabilized by the presence of two π -donor nitrogen atoms bonded to the carbene carbon atom. The synthesis of the first push-pull phosphanylsilylcarbene of formula $(\text{R}_2\text{P})(\text{SiMe}_3)\text{C}$ ($\text{R} = \text{NiPr}_2$) by Bertrand and co-workers was also a milestone in carbene chemistry.^[3] Mixed-substituent aminophosphanylcarbenes have recently been prepared.^[4] Of great interest are also the analogous diphosphanylcarbenes $(\text{R}_2\text{P})_2\text{C}$, although they are only known as transient species,^[5] which have been investigated by ab initio calculations.^[6] Interestingly, their protonated phosphoniumphosphanylcarbene derivatives $[(\text{R}_2\text{P})(\text{R}_2\text{PH})\text{C}]^+$ ions are known to be stable.^[7]

We report herein on the generation and trapping reactions of the transient highly electrophilic metalladiphosphanylcarbene $[\text{Ru}(\text{CNtBu})_4(\text{PPh}_2)_2\text{C}]^{2+}$ (**2**).^[8] The electrophilic character of **2** has been confirmed experimentally and by density functional theory (DFT) calculations.^[9]

Transient carbene **2** is formed from the cationic complex $[\text{Ru}(\text{CNtBu})_4\{(\text{PPh}_2)_2\text{CI}\}]^+$ (**1**)^[10] by iodide abstraction with

through the phosphorus atoms avoids dimerization to form the corresponding $1\lambda^5,3\lambda^5$ -diphosphete derivative,^[11] or even 1,2-migration of a phenyl group to give the phosphalkene,^[5b] and enhances the electrophilicity of the carbene as the phosphorus lone pairs can no longer be used for π donation to the carbene carbon atom. Owing to its high electrophilicity (see calculated electron affinities (EA) values in Table 1) **2** is

Table 1: Calculated structural parameters, singlet–triplet splittings (ΔE_{ST}), and electron affinities (EA) of **2b**.

	B3LYP6- 31G*,LanL2DZ ^[a]	B3LYP6- 31G*,3- 21G	B3LYP6- 31G*,3- 21G*	B3LYP6- 311++G*,3- 21+G*
C–P [Å]	1.673	1.681	1.682	1.662
P–C–P [°]	134.3	129.2	129.3	137.9
ΔE_{ST} [kcal mol ^{−1}]	−8.96	−9.86	−10.00	−10.80
EA [eV]			8.94	8.99

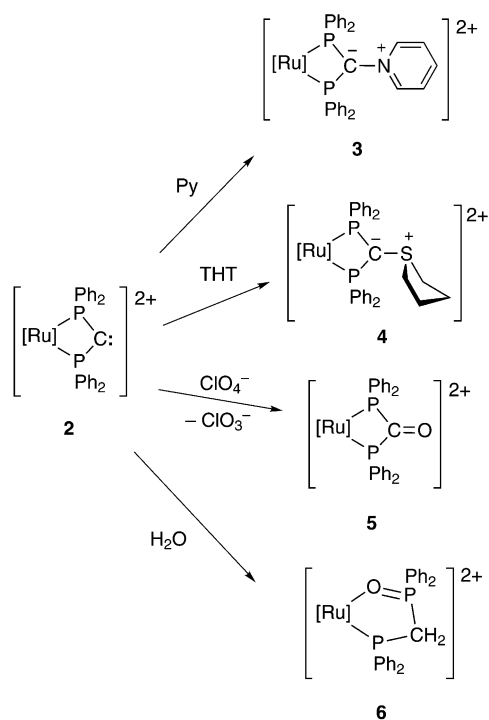
[a] Second basis for Ru, first basis for all the other atoms.

very unstable and instantaneously decomposes, unless a trapping reagent is added. Thus, reaction of **1** with AgBF_4 in CH_2Cl_2 as solvent in the presence of pyridine (Py) gives complex **3**, the pyridine adduct of carbene **2** (Scheme 2).^[12] Complex **3** cocrystallizes with the silver complex salt $[\text{Ag}(\text{Py})_2]\text{BF}_4$ giving suitable crystals for X-ray analysis (Figure 1).^[13] In the new pyridinium diphosphanylylide ligand the C1–N1 bond is slightly shortened with respect to single bond, and the pyridinium plane is coplanar with the P1–P2–C1 plane allowing a π interaction of the ylide carbon atom C1 with the π system in the ring. The P1–C1 and P2–C1 bonds are appreciable shorter than single bonds indicating that the negative charge at the ylide carbon atom is also shared with both coordinated phosphorus atoms, thus stabilizing the ylide structure. Another adduct of carbene **2** is formed by treatment of **1** with AgBF_4 in the presence of tetrahydrothiophene (tht). The reaction occurs readily to give complex **4** (Scheme 2).^[14] The ^1H NMR spectrum of **4** shows three resonance signals for the CH_2 groups of tht (see Experimental Section), as the two protons of each $\alpha\text{-CH}_2$ unit are inequivalent owing to its different orientation respect to the

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Scheme 2. Trapping reactions of carbene **2**. [Ru] = [Ru(CNtBu)₄], tht = tetrahydrothiophene.

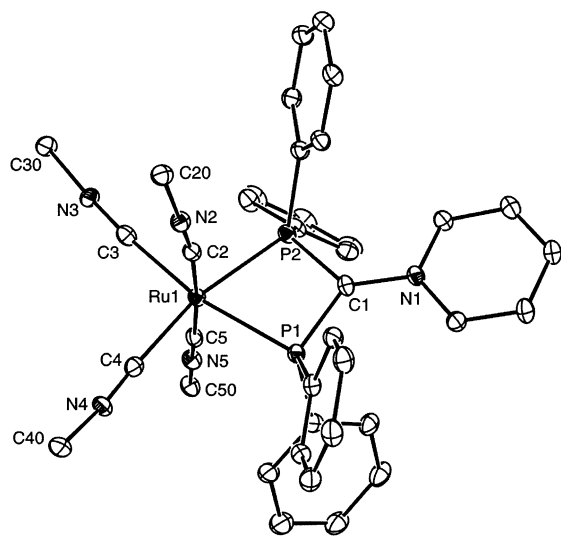


Figure 1. A view of the structure of the cation **3** (thermal ellipsoids set at 20% probability). Methyl groups in the CNtBu ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1-P1 2.355(2), Ru1-P2 2.359(2), P1-C1 1.761(9), P2-C1 1.756(10), N1-C1 1.428(10); P1-Ru1-P2 70.48(9), N1-C1-P2 128.9(7), N1-C1-P1 129.8(7), P2-C1-P1 101.3(4).

lone pair of sulfur. The solid-state structure of **4** was solved by X-ray analysis (Figure 2), and clearly shows a tht solvent molecule stabilizing carbene **2** with a rather strong C–S interaction (C1–S1 1.707(6) Å).

When carbene **2** is generated by treatment of **1** with an excess of AgClO₄, the diphosphanlyketone complex

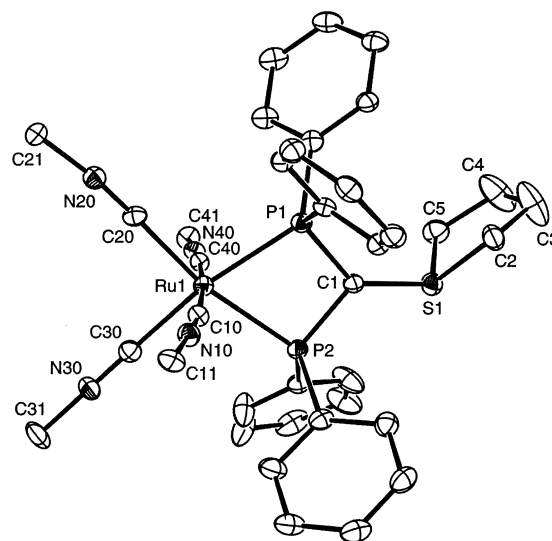
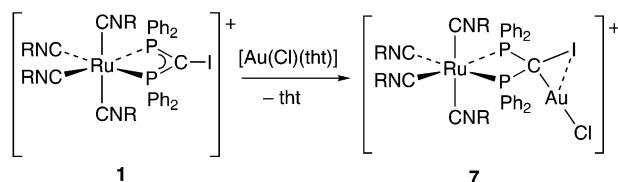


Figure 2. A view of the structure of the cation **4** (thermal ellipsoids set at 20% probability). Methyl groups in the CNtBu ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.774(6), P2–C1 1.771(6), S1–C1 1.707(6), S1–C2 1.820(7), S1–C5 1.812(7); P1–Ru1–P2 70.51(5), S1–C1–P2 124.5(3), S1–C1–P1 134.9(4), C1–S1–C2 114.2(3), C1–S1–C5 109.8(3).

[Ru(CNtBu)₄](PPh₂)₂C=O]²⁺ (**5**) is obtained, after precipitation of AgI (Scheme 2). This result implies the transfer of an oxygen atom from the ClO₄[−] group to the transient carbene **2**, which probably proceeds through nucleophilic attack of the oxoanion to the carbene carbon atom. The IR spectrum of **5** reveals the presence of the ketone group (ν_{CO} = 1721 cm^{−1} (m)), as well as the ¹³C{¹H} NMR spectrum which shows a triplet at δ = 216.6 ppm (¹J(P,C) = 16 Hz) for the P₂CO carbon atom.^[15] The solid structure of **5** has also been confirmed by X-ray analysis (not shown).

The formation of carbene **2** by treatment of **1** with AgBF₄ in the presence of H₂O yields the cationic complex [Ru(CNtBu)₄](O=PPh₂)(PPh₂CH₂)²⁺ (**6**; Scheme 2), which contains a mono-oxidized methylenebis[(diphenyl)phosphane] (dppm) ligand arising from activation of both O–H bonds in the water molecule by the carbene. The structure of **6** has been confirmed by ³¹P and ¹H NMR spectroscopy (see Experimental Section) and by X-ray analysis. On the basis of the known trapping reactions of transient diphosphanlycarbenes with alcohols,^[5a] the formation of **6** could proceed through insertion of carbene **2** into a O–H bond of water, followed by a 1,2-shift of the OH group to a phosphorus atom and further proton migration to the central carbon atom.

To investigate the iodide abstraction leading to carbene **2** we treated **1** with some soluble silver(i) and gold(i) complexes. With the silver derivative Ag(ClO₄)(PPh₃), the interaction with iodide is so strong that formation of [[AgI(PPh₃)₄]] is immediately observed with parallel formation of [Ru(CNtBu)₄](PPh₂)₂C²⁺ as decomposition product of the carbene. Fortunately, treatment of **1** with [AuCl(tht)] allowed the isolation of the complex [Ru(CNtBu)₄(PPh₂)₂C(AuCl)I]⁺ (**7**; Scheme 3). The structure of this cation (Figure 3) shows the AuCl unit bonded to the methanide carbon atom, but also a close Au⋯I contact of 3.35 Å which is shorter than the sum of



Scheme 3. Formation of the heterometallic ruthenium(II)/gold(I) complex **7**. R = *t*Bu.

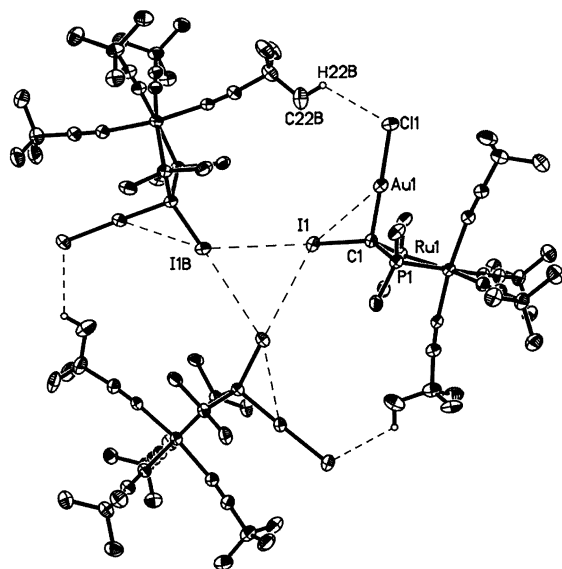


Figure 3. A view of the structure of the cation **7** (thermal ellipsoids set at 20% probability) showing a three-cation aggregate. Phenyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–C1 2.100(19), Au1–Cl1 2.326(5), C1–I1 2.171(18), C1–P1 1.837(12); P1–Ru1–P1 71.48(18), C1–Au1–Cl1 178.7(5), P1–C1–P1 97.4(9), P1–C1–Au1 104.4(7), P1–C1–I1 122.4(6), Au1–C1–I1 103.7(8).

van der Waals radii of both atoms (3.64 Å). Some activation is also observed in the C–I bond in **7** (2.177(18) Å) compared to coordinated diphosphaniodomethanide (2.115(4) Å).^[16] All these structural data indicate that **7** can be considered an isolated intermediate for the formation of transient carbene **2** by halide abstraction from **1** with metal fragments. Additionally the solid structure of **7** is of interest in forming supramolecular triangular aggregates, with central I...I contacts and peripheral C–H...Cl hydrogen bonds (Figure 3).

Table 1 shows some selected results of the calculations performed on the carbene [Ru(CNH)₄(PH₂)₂C]²⁺ (**2b**), a model structure obtained from **2** by replacing *t*Bu and Ph substituents by hydrogen atoms.^[9] The optimized structure shows a perfect C_{2v} symmetry in the highest levels of calculation, both for singlet and triplet states, although for the triplet state P–C distances are clearly longer (1.788 Å) and P–C–P angles are much smaller (113.1°) than for the singlet ground state (the values of which are shown in Table 1). These results are much in line with those found for other symmetrically substituted cyclic diphosphanylcarbenes,^[6b] and clearly differ from symmetrically substituted acyclic diphosphanylcarbenes,^[6a] which prefer an asymmetric P–C multiple-bond phosphorus vinyl ylide structure.

In conclusion we have present an approach to generate a unique dicationic singlet carbene (**2**), whose electrophilic character has been confirmed experimentally and by DFT calculations. This new type of carbene, as well as its isolated pyridine and tetrahydrothiophene adducts, show promise as reaction intermediates for the preparation of new functionalized diphosphane ligands, as exemplified with the synthesis of the diphosphanylketone derivative **5**.

Experimental Section

All reactions and manipulations were performed under an atmosphere of dry nitrogen by using standard Schlenk and glovebox techniques. Solvents were distilled over appropriate drying agents under dry nitrogen prior to use. Chemical shifts of the NMR spectra are referenced to internal SiMe₄ (¹H and ¹³C) or external H₃PO₄ (³¹P).

3-(BF₄)₂·0.5[[Ag(Py)₂]BF₄]: Pyridine (81 μL, 1 mmol) was added to a solution of [Ru(CN*t*Bu)₄[(PPh₂)₂Cl]] (**1-I**; 0.11 g, 0.1 mmol) in CH₂Cl₂ (20 mL). This solution was transferred by canula to a Schlenk containing AgBF₄ (0.08 g, 0.4 mmol) previously cooled to –75 °C and covered to protect from the light. The mixture was stirred for 10 min and then allowed to warm to room temperature and stirred for a further hour. Filtration of the mixture gave a clear yellow solution. Half of the solvent was removed in vacuo and diethyl ether (15 mL) was carefully added. Storage at –18 °C for 4 days afforded yellow crystals, yield: 0.094 g (67%). Elemental analysis (%) calcd for C₅₅H₆₆N₇Ag_{0.5}B_{2.5}F₁₀N₆P₂Ru: C 53.05, H 5.34, N 6.75; found: C 52.53, H 5.10, N 6.77; IR (CH₂Cl₂): $\tilde{\nu}$ = 2215 (w), 2180 cm^{–1} (s) (CN*t*Bu); ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 10.5 ppm; ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.1–7.3 (35H), 1.53 (s, 18H, CN*t*Bu), 0.95 ppm (s, 18H, CN*t*Bu); ¹³C NMR (75.5 MHz, CD₂Cl₂): δ = 133.5–126.3 (Ph and Py), 59.7 (s, CNC(CH₃)₃), 59.0 (s, CNC(CH₃)₃), 61.8 (t, ¹J(P,C) = 49, P₂CPh), 30.7 (s, CNC(CH₃)₃), 29.9 ppm (s, CNC(CH₃)₃). Resonance for CNC(CH₃)₃ not observed.

4-(BF₄)₂: A solution of **1-I** (0.1 g, 0.093 mmol) and THT (1 mL) in THF (30 mL) was added through a canula to a Schlenk containing AgBF₄ (0.062 g, 0.318 mmol). The mixture was stirred for 20 min and then filtered and the filtrate concentrated to 15 mL to afford white crystals of the compound, yield: 0.056 g (56%). Elemental analysis (%) calcd for C₄₉H₆₄N₄B₂F₈P₂RuS: C 54.61, H 5.99, N 5.20; Found: C, 54.32; H, 5.96; N, 5.09; IR (CH₂Cl₂): $\tilde{\nu}$ = 2214 (m), 2172 cm^{–1} (vs) (CN*t*Bu); ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 0.38 ppm; ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.7–7.6 (20H, Ph), 3.46 (m, 2H, tht), 1.85 (m, 2H, tht), 1.82 (m, 4H, tht), 1.55 (s, 18H, CN*t*Bu), 1.15 ppm (s, 18H, CN*t*Bu).

5-(ClO₄)₂: AgClO₄ (0.025 g, 0.12 mmol) was added to a solution of **1-I** (0.05 g, 0.048 mmol) in CH₂Cl₂ (10 mL). The mixture was stirred for 10 min in the absence of light. After filtration, the solvent was removed from the filtrate in vacuo and the residue recrystallized from CH₂Cl₂/diethyl ether affording yellow crystals, yield: 0.036 g (73%). Elemental analysis (%) calcd for C₄₅H₅₆N₄Cl₂O₈P₂Ru: C 52.43, H 5.47, N 5.43; Found: C, 52.35; H, 5.31; N, 5.29; IR (CH₂Cl₂): $\tilde{\nu}$ = 2230 (w), 2190 cm^{–1} (s) (CN*t*Bu), 1721 cm^{–1} (m) (CO); ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 76.2 ppm; ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.8–7.4 (20H, Ph), 1.76 (s, 18H, CN*t*Bu), 0.95 ppm (s, 18H, CN*t*Bu); ¹³C NMR (75.5 MHz, CD₂Cl₂): δ = 134–126 (Ph), 216.6 (t, ¹J(P,C) = 16 Hz) P₂CO, 61.4 (s, CNC(CH₃)₃), 60.6 (s, CNC(CH₃)₃), 30.5 (s, CNC(CH₃)₃), 29.3 ppm (s, CNC(CH₃)₃). Resonance for CNC(CH₃)₃ not observed.

6-(BPh₄)₂: A solution containing **1-I** (0.09 g, 0.08 mmol) and water (4 μL, 0.22 mmol) in CH₂Cl₂ (20 mL) was added through a canula to AgBF₄ (0.08 g, 0.4 mmol) placed in a Schlenk previously cooled to –75 °C and covered from the light. The mixture was stirred for 10 min and then allowed to warm to room temperature and stirred for a further hour. Filtration of the solution and evaporation of the solvent from the filtrate afforded a white solid of **6**-(BF₄)₂. Yield:

0.086 g (70 %). To obtain suitable crystals for an X-ray diffraction study, a metathesis of the anion was performed by treating a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution of the compound with an excess of NaBPh_4 . Elemental analysis (%) calcd for $\text{C}_{93}\text{H}_{98}\text{N}_4\text{B}_2\text{OP}_2\text{Ru}$: C 75.86, H 6.70, N 3.80; Found: C 75.79; H 6.45, N 4.02; IR (CH_2Cl_2): $\tilde{\nu} = 2223$ (w), 2181 (s), 2164 cm^{-1} (sh) (CNtBu); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 67.7$ (d, $^2J(\text{P,P}) = 29$ Hz), 41.4 ppm (d, $^2J(\text{P,P}) = 29$ Hz); ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.0\text{--}7.4$ (60H, Ph), 4.01 (dd, $^2J(\text{P,H}) = 11$, $^2J(\text{P,H}) = 9$ Hz, 2H, CH_2), 1.73 (s, 9H, CNtBu), 1.53 (s, 9H, CNtBu), 1.10 ppm (s, 18H, CNtBu).

7-[Au(Cl)(I)]: [Au(Cl)(tht)] (0.031 g, 0.096 mmol) was added to a solution of **1-I** (0.050 g, 0.048 mmol) in THF (12 mL) and the resulting mixture stirred for 10 min. The solution was then concentrated to 6 mL and let to stand over night to afford yellow crystals, yield: 0.065 g (90 %). IR (CH_2Cl_2): $\tilde{\nu} = 2215$ (s), 2177 cm^{-1} (vs) (CNtBu); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 13.4$ ppm; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.7\text{--}7.4$ (20H, Ph), 1.63 (s, 18H, CNtBu), 1.44 (s, 9H, CNtBu), 0.99 ppm (s, 9H, CNtBu).

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for 322 parameters. CCDC-187344 (**3**), CCDC-211797 (**4**), CCDC-187345 (**5**), and CCDC-211798 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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; or deposit@ccdc.cam.ac.uk).

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