Synthons for carbide complex chemistry†

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The sterically accessible carbide complex, $(\text{Cy}_3\text{P})\text{Cl}_3\text{Ru}\equiv\text{C}-\text{PtCl}(\text{py})_2$, acts as a synthon for terminal and bridging carbide fragments that relocate to pincer and A-frame scaffolds upon ligand addition. This concept, benefitting from coordination sphere selection as the concluding step, confronts traditional synthetic strategies and broadens the scope for carbide complexes.

While multiply-bonded ligands such as nitride and oxide are available *via* simple N and O atom transfer reactions, simple C atom transfer reactions are virtually¹ absent as entries to molecular carbides. In a few instances, C atom insertion into metal–ligand bonds have been reported.² In principle, CH group transfer reactions³ offer carbide complexes upon deprotonation. Still, predominantly, splitting of metal-coordinated carbon ligands⁴ leaves carbide units embedded in substitutionally inert ligand spheres, producing structurally conserved $\text{M}\equiv\text{C}$ ⁵ and $\text{M}=\text{C}=\text{M}$ ⁶ families. Though carbide complexes are amenable to metallation⁷ and halide exchange,⁸ these strategies offer modest structural variability. Labile carbide complexes, in contrast, could bypass these shortcomings by allowing the net transfer of $\text{M}\equiv\text{C}$ or $\text{M}=\text{C}=\text{M}$ groups. Being notoriously susceptible to interception, such transferable carbide fragments have eluded isolation. These fragments would nonetheless have potential relevance to substrate conversion by nitrogenases⁹ and Fischer–Tropsch process catalysts.¹⁰

Though reaction of the terminal ruthenium carbide complex, $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}$ (**RuC**, Cy = cyclohexyl), with non-metal fragments¹¹ occasionally induces ligand migration,¹² metallation invariably leaves an intact **RuC** coordination sphere,^{13,14} *i.e.* $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}[\text{M}]$. In **RuC**, associative phosphine substitution pathways are unlikely due to the steric bulk of the PCy_3 ligands.

Computationally, Johnson¹⁵ found that large energetic penalties block dissociative pathways as well. Here, we report a sterically accessible mono-phosphine complex, $(\text{Cy}_3\text{P})\text{Cl}_3\text{Ru}\equiv\text{C}[\text{Pt}]$, which reacts readily with ligands by expulsion of PCy_3 and at times $[\text{Pt}]$. This enables insertion of $\text{Ru}\equiv\text{C}-\text{Pt}$ and $\text{Ru}\equiv\text{C}$ groups in A-frame and pincer scaffolds that, despite ubiquity, are unprecedented in carbide chemistry. The net transfer of carbide groups addresses the viability of transferable carbide fragments and introduces an appealing strategy for synthesizing carbide complexes, requiring selection of supporting ligands rather than compliance with thermodynamic dictate.

In an investigation of the nucleophilicity of **RuC**, we examined reactions with the standard reference complex, *trans*- $\text{PtCl}_2(\text{py})_2$ (py = pyridine). ¹³C NMR revealed a bridging carbide resonance with ¹⁹⁵Pt satellites (354.6 ppm, *J* = 1372 Hz), but rather than a central triplet expected for $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}[\text{Pt}]$ products, a central doublet (*J* = 13 Hz) indicated the loss of PCy_3 . X-ray diffraction uncovered the carbide-bridged complex, $(\text{Cy}_3\text{P})\text{Cl}_3\text{Ru}\equiv\text{C}-\text{PtCl}(\text{py})_2$ (**Py₂RuCPt**, Scheme 1 and Fig. 1), as well as the salt *trans*- $[\text{PtCl}(\text{py})_2(\text{PCy}_3)]\text{Cl}$ (*cf.* ESI†). Thereby, *trans*- $\text{PtCl}_2(\text{py})_2$ reacts both as a metallation reagent and a phosphine scavenger, yielding **Py₂RuCPt** as air-stable crystals in near-quantitative isolated yields (97%). When equimolar amounts of **RuC** and *trans*- $\text{PtCl}_2(\text{py})_2$ react, **Py₂RuCPt** forms in 50% yield, leaving half the **RuC** unconverted. This emphasizes the unique reactivity of *trans*- $\text{PtCl}_2(\text{py})_2$ towards **RuC** as compared to other metal fragments.^{13,14} Structurally, **Py₂RuCPt** parallels Johnson's arylcarbyne, $(\text{Cy}_3\text{P})\text{Cl}_3\text{Ru}\equiv\text{C}(p\text{-C}_6\text{H}_4\text{CH}_3)$,¹⁶ and Grubbs' homometallic $[\text{Ru}\equiv\text{C}-\text{Ru}]$ complex.¹⁷ Bond distances along the $\text{Ru}\equiv\text{C}-\text{Pt}$ spine mirror known $\text{Ru}\equiv\text{C}-\text{Pt}$ fragments¹⁴ (Table 1), whereas the carbide bridge is unusually bent. Steric

Scheme 1 Synthesis of **Py₂RuCPt**.

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Fig. 1 Molecular structure of **py₂RuCPt** with thermal ellipsoids at 50% probability. Hydrogen atoms and co-crystallized CH₂Cl₂ are omitted.

Table 1 Selected bond distances (Å) and angles (°)

Complex	Ru–C	Pt–C	Ru–C–Pt
py₂RuCPt	1.669(1)	1.900(1)	166.24(9)
dppm₂RuCPt ^a	1.698(2)	1.852(2)	177.0(2)
	1.692(4)	1.853(4)	180
dcpm₂RuCPt	1.694(2)	1.842(2)	166.2(1)
Ad^{PNP}RuC	1.648(3)	—	—

^a Crystallizes in both a triclinic and a monoclinic space group.

repulsion between the pyridine rings and the PCy₃ ligands partly explains the bent geometry (the shortest intramolecular separation between pyridine and PCy₃ is 2.832 Å). Moreover, additional π -backdonation from filled Pt d_{z²} orbitals into **RuC** π^* orbitals¹⁸ is only symmetry-allowed for bent geometries. Yet, the most important structural feature of **py₂RuCPt** is the steric accessibility at ruthenium. This alludes to the potential for displacing the remaining PCy₃ ligand, ultimately transferring the carbide fragment to new ligand scaffolds.

The ability of diphosphinomethanes to harbour linear oxo-bridged metal complexes¹⁹ inspired the deployment of CH₂(PPh₂)₂ (dppm, Ph = phenyl) as a supporting ligand for the Ru $\equiv$ C–Pt spine. Indeed, dppm smoothly converts **py₂RuCPt** to (μ-dppm)₂Cl₃Ru $\equiv$ C–PtCl (**dppm₂RuCPt**, Scheme 2 and Fig. 2). In solution, **dppm₂RuCPt** produces a precipitate with BPh₄[−], and in the gas phase, electrospray ionization mass spectrometry (ESI-MS) reveals an intense monocation (as well as di- and trications) with *m/z* ratios corresponding to the loss of one chloride. These features attest to the lability and contact ion pair behaviour of the chloride *trans* to the bridging carbide ligand. ¹³C NMR reveals the carbide ligand as a triplet of triplets at 361.9 ppm due to coupling to two pairs of equivalent

Fig. 2 Molecular structures of **dppm₂RuCPt** (left) and **dcpm₂RuCPt** (right), with thermal ellipsoids at 50% probability. Hydrogen atoms, disordered parts, and co-crystallized solvent molecules are omitted.

Table 2 NMR coupling constants (Hz) for A-frame complexes

Nuclei	dppm₂RuCPt	dcpm₂RuCPt	Nuclei	dppm₂RuCPt	dcpm₂RuCPt
Pt–C	913	970	C–RuP	17.9 ^a	14.4 ^a
Pt–RuP	116	120	C–PtP	10.2 ^a	9.3 ^a
Pt–PtP	2614	2482	PtP–RuP	4.9 ^a	0

^a Averaged.

phosphorus nuclei, and further coupling to ¹⁹⁵Pt produces satellite peaks (Table 2). Both the Ru-bound (^{Ru}P) and the Pt-bound (^{Pt}P) phosphorus nuclei display large coupling constants to Pt, to the ¹³C-labelled carbide, and to each other. The coupling of nuclear spins indicates electronic delocalization across the A-frame complex, which sets **dppm₂RuCPt** apart from typical Ru $\equiv$ C–Pt complexes.¹⁴

Replacement of dppm by its saturated analogue, CH₂(PCy₂)₂ (dcpm), allows evaluation of changes in steric and electron-donating abilities of the diphosphine ligands. Upon reaction with two equivalents of dcpm, **py₂RuCPt** readily associates with the first dcpm ligand, forming a [(μ-dcpm)(Cy₃P)Ru $\equiv$ C–Pt] intermediate (identified by NMR, Scheme 2, cf. ESI[†]). However, the ensuing formation of (μ-dcpm)₂Cl₃Ru $\equiv$ C–PtCl (**dcpm₂RuCPt**) is only complete within days at room temperature, reflecting the steric congestion of dcpm. On standing, the [(μ-dcpm)(Cy₃P)Ru $\equiv$ C–Pt] intermediate rearranges to (μ-dcpm)Cl₃Ru $\equiv$ C–PtCl(PCy₃) *via* migration of the PCy₃ ligand from Ru to Pt (identified by X-ray crystallography, cf. ESI[†]). This observation suggests formation of **py₂RuCPt** (*vide supra*) to proceed with initial RuC–Pt bond formation followed by departure of PCy₃ *via* Pt; on the other hand, initial dissociation of PCy₃ from **RuC** followed by coordination of Pt to a reactive {Ru $\equiv$ C} unit seems improbable.¹⁵

Scheme 2 Synthesis of **dppm₂RuCPt** and **dcpm₂RuCPt**.

Scheme 3 Synthesis of $\text{Ph}_3\text{P,Cy}_3\text{PRuC}$ and AdPNPRuC .

With dcpm being a stronger σ -donor ligand than dppm , increased s -character in bonding would plausibly produce larger NMR coupling constants in $\text{dcpm}_2\text{RuCPt}$ than in $\text{dppm}_2\text{RuCPt}$. However, this is only the case for $J_{\text{Pt-C}}$ (Table 2). Instead, the $J_{\text{Pt-RuP}}$ display similar magnitudes, while the remaining coupling constants are larger in $\text{dppm}_2\text{RuCPt}$ than in $\text{dcpm}_2\text{RuCPt}$. In fact, line widths obscure $J_{\text{RuP-PtP}}$ in $\text{dcpm}_2\text{RuCPt}$, despite comparable bond metrics for the central $\{\text{PCH}_2\text{P}\}$ groups.

The solid-state structures reconcile observations from NMR; both A-frame complexes display very short carbide-platinum bonds (shortest 2.2–2.9% C–Pt bonds in the Cambridge Structural Database, CSD v. 1.19), suggesting the diphosphine ligands to constrict the $\text{Ru}\equiv\text{C-Pt}$ spines. Notably, $\text{dcpm}_2\text{RuCPt}$ displays the shortest Pt–C bond and the largest Pt–C coupling constant. The carbide bridges also display angular diversity with $\text{dppm}_2\text{RuCPt}$ being linear and $\text{dcpm}_2\text{RuCPt}$ being bent (166.2° , cf. ESI† for discussion); consequently, small coupling constants and ineffective delocalization accompany puckering at the carbide bridge. The Ru–Pt separations (3.51–3.55 Å) are smaller than Re–Re and Os–Os separations (3.58–3.83 Å) in oxo bridged A-frame complexes,¹⁹ indicating the carbide bridges to be strong. In addition, the bridging carbide ligands exert large structural *trans* influences. This produces long Ru–Cl bonds (>2.5 Å) *trans* to the $\text{Ru}\equiv\text{C-Pt}$ vector, which accounts for the observed contact ion pair behaviour (*vide supra*).

Another synthetic function of Py_2RuCPt lies in its potential for affording terminal carbide complexes. While RuC is unreactive towards PPh_3 , treatment of Py_2RuCPt with PPh_3 provides $(\text{Ph}_3\text{P})(\text{Cy}_3\text{P})\text{Cl}_2\text{Ru}\equiv\text{C}$ ($\text{Ph}_3\text{P,Cy}_3\text{PRuC}$) along with py and $\text{cis-PtCl}_2(\text{PPh}_3)_2$ (Scheme 3). The carbide ^{13}C resonance appears at 473.6 ppm, and the phosphines adopt a *trans* disposition ($J_{\text{P-P}} = 249$ Hz). However, $\text{Ph}_3\text{P,Cy}_3\text{PRuC}$ decomposes in solution, likely due to poor electron donation from PPh_3 that also prevents the formation of $(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}$ from Grubbs' catalyst *via* olefin metathesis.¹³

Pincer ligands stabilize terminal $\text{M}\equiv\text{N}$ units with four, five, and six-coordination²⁰ and could possibly protect terminal $\text{Ru}\equiv\text{C}$ units. Thus, reaction of Py_2RuCPt with two equivalents of $\text{HN}(\text{CH}_2\text{CH}_2\text{PAD}_2)_2$ (AdPNP , $\text{Ad} = 1\text{-adamantyl}$) provides $[(\text{AdPNP})\text{ClRu}\equiv\text{C}]\text{Cl}$ (AdPNPRuC , Scheme 3, Fig. 3). ^{13}C NMR reveals a terminal carbide resonance at 479.1 ppm with very small coupling constants to phosphorus, indicating an electronically isolated $\text{Ru}\equiv\text{C}$ unit. Along with AdPNPRuC , carbide resonances from RuC and $[(\text{AdPNP})\text{ClRu}\equiv\text{C-PtCl}(\text{py})_2]\text{Cl}_2$ arise (AdPNPRuCPt , cf. ESI†). The persistence of the Ru–C–Pt bond indicates the potential of AdPNPRuC to serve as a ligand, and apparently, the

Fig. 3 Molecular structure of AdPNPRuC with thermal ellipsoids at 50% probability. Hydrogen atoms (except NH) and co-crystallized CHCl_3 are omitted.

formation of AdPNPRuC proceeds by exclusive association of the first AdPNP at Ru, while the second AdPNP equivalent provokes the departure of Pt. This contrasts with the formation of the A-frame complexes that proceeds *via* diphosphine-bridged metal centres. The central triple bond in AdPNPRuC is extremely short (shortest 0.02% Ru–C bonds in the CSD), but not significantly perturbed by the formal replacement of chloride for a ligating amine. Hydrogen bonding between the amine and a second coordination sphere chloride are in line with the formation of a cationic fragment, $(\text{AdPNP})\text{ClRu}\equiv\text{C}^+$ (ESI-MS). The amine in AdPNPRuC is relatively acidic and deprotonates upon isolation from ethanol; thus, the prevalence of AdPNPRuC as its carbide-amine tautomer over a carbyne-amine tautomer reflects the stability of the $\text{Ru}\equiv\text{C}$: fragment buried within the pincer ligand.

The isolation of Py_2RuCPt provides a sterically accessible carbide fragment, readily exchanging ligands around its $\text{Ru}\equiv\text{C-Pt}$ core. For the first time, this enables $\text{M}\equiv\text{C}$ group transfer reactions as a strategy for designing carbide complexes. Simple selection of ligands governs the coordination environment and the electronic structure in the resulting terminal and bridging carbide complexes, demonstrating the flexibility of the approach. Generation of Py_2RuCPt requires a common metallation reagent and proceeds in near-quantitative yields under atmospheric air. Thus, the present report of A-frame ($\text{Ru}\equiv\text{C-Pt}$) and pincer ($\text{Ru}\equiv\text{C}$) complexes ushers in a facile concept for manipulating carbide complexes, and we are currently extending²¹ the chemistry to new transition metal and main group fragments.

Conflicts of interest

There are no conflicts to declare.

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- 21 See ESI† for $^{102}\text{RuCpt}$ analogues (using *trans*-PdCl₂(py)₂ or *trans*-PtCl₂(Hpz)₂, Hpz = pyrazole).