

Iodine Adducts

International Edition: DOI: 10.1002/anie.201606551
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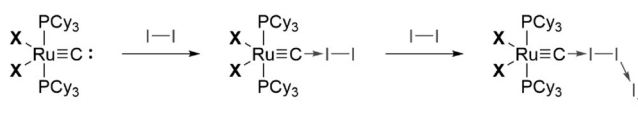
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Abstract: The terminal carbide ligands in $[(\text{Cy}_3\text{P})_2\text{X}_2\text{Ru}\equiv\text{C}]$ complexes (X = halide or pseudohalide) coordinate molecular iodine, affording charge-transfer complexes rather than oxidation products. Crystallographic and vibrational spectroscopic data show the perturbations of iodine to vary with the auxiliary ligand sphere on ruthenium, demonstrating the σ -donor properties of carbide complexes to be tunable.

The electronic structure of terminal transition-metal carbide complexes is isolobal^[1] to that of carbon monoxide.^[2] This suggests that these entities engage in similar bonding interactions with transition-metal centers, acting as σ -donor and π -acceptor ligands. While carbon monoxide is unalterable and internally highly stable, manipulation of the electronic structure at $\text{M}\equiv\text{C}$ fragments through ligand-sphere selection is enticing. Thus, theory^[2,3] suggests that $\text{M}\equiv\text{C}$ units represent tunable analogues of CO. The π -accepting properties of $\text{Ru}\equiv\text{C}$ ligands are established experimentally.^[4] By contrast, studies of σ -donor properties of $\text{M}\equiv\text{C}$ complexes and their relationship to the metal coordination environment are limited to computation. This information, however, is relevant to small-molecule activations harnessing carbide ligands: CO-derived terminal carbide ligands enable Fischer–Tropsch chemistry,^[5] and N_2 reduction in nitrogenases involves interstitial carbide ligands.^[6] These transformations pose fundamental questions about the properties of carbide ligands and carbide complexes and motivate investigations into their chemistry.

$\text{Mo}\equiv\text{C}$,^[7] $\text{W}\equiv\text{C}$,^[8] $\text{Ru}\equiv\text{C}$,^[9] $\text{Os}\equiv\text{C}$,^[10] and Ru_2C ^[11] containing complexes open several avenues to synthetic chemists. Nestled within protective ligand spheres, the carbide ligands react with metal complex fragments to form bimetallic bridges, though without joining several metal centers into carbide-centered clusters.^[4,9b,12] On the other hand, the integrity of the carbide complexes is typically disrupted on association with non-metal fragments,^[7b–d,8,9c–g,10,13] which induce geometric changes opposing the structural similarity upon metalation. Starting from terminal ruthenium carbide complexes derived from Grubbs' catalyst,^[9a,b,e] we have developed selective substitution reactions for varying X in $[(\text{Cy}_3\text{P})_2\text{X}_2\text{Ru}\equiv\text{C}]$ (X_2RuC ; Cy = cyclohexyl, X = halide or pseudohalide; in the case of mixed X ligands, one ligand is

always chloride, and these complexes are denoted by X_2RuC).^[9g] These complexes coordinate to elemental iodine in a σ -donor fashion to form charge-transfer complexes $[(\text{Cy}_3\text{P})_2\text{X}_2\text{Ru}\equiv\text{C}\rightarrow\text{I}-\text{I}]$ ($\text{X}_2\text{RuC}\rightarrow\text{I}_2$, Scheme 1), which recalls similar reactions of phosphines.^[14] Buried between the bulky



Scheme 1. Formation of charge-transfer complexes between X_2RuC complexes and I_2 .

Cy_3P ligands, the X ligands influence the electronic structure at the $\text{Ru}\equiv\text{C}$ terminus while its steric profile remains conserved. Hence, the question of electronic tunability of $\text{M}\equiv\text{C}$ ligand σ -donor properties is addressed through ligand-sphere manipulation.

In contrast to the tungsten complex $[(\text{Tp}')(\text{OC})_2\text{W}\equiv\text{C}\text{Li}]$ (Tp'^- = hydridotris(3,5-dimethylpyrazol-1-yl)borate), which forms an iodocarbene on reaction with I_2 ,^[8] the corresponding reactions of X_2RuC complexes are stalled at the stage of charge-transfer complexes. Clean conversions in solution are witnessed by ^{13}C -NMR spectroscopy, showing carbide resonances slightly upfield (by 0.2–10 ppm) relative to those of the parent carbide complexes. The association constants are fairly large as stoichiometric reactions appear quantitative based on NMR data, and UV/Vis spectroscopy shows $\text{X}_2\text{RuC}\rightarrow\text{I}_2$ to prevail in the > 1 mM concentration range (Figure S11 in the Supporting Information). While the complexes start decomposing within hours in solution, they are stable as orange to dark-red crystals. Figure 1 shows the molecular structure of $\text{Cl}_2\text{RuC}\rightarrow\text{I}_2$ (for the remaining complexes see the Supporting Information).

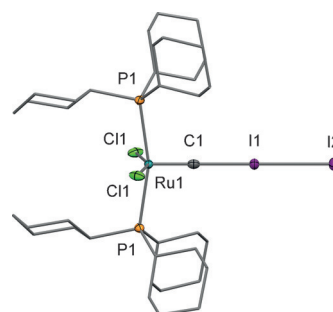


Figure 1. Molecular structure of $\text{Cl}_2\text{RuC}\rightarrow\text{I}_2$. Thermal ellipsoids correspond to the 50% probability level. H atoms are omitted, and cyclohexyl groups are shown as wireframe.

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The $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes crystallize in the space group $C2/c$ with the $\text{Ru} \equiv \text{C} \rightarrow \text{I}-\text{I}$ unit having crystallographic linear geometry and ruthenium retaining its square-pyramidal geometry. The slight elongation of the strong $\text{Ru} \equiv \text{C}$ bond (0.6–1.4 %), together with the relatively large separation between the carbide ligand and iodine, suggest a moderate strength of interaction (Table 1). However, the I–I bond

Table 1: Interatomic distances [Å] for $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ and X_2RuC complexes.

Complex	Ru1–C1 ^[a]	C1–I1	I1–I2	C1–I2
(NC) $_2\text{RuC} \rightarrow \text{I}_2$	1.659(2) [1.636(3)]	2.285(2)	2.8607(3)	5.146
$\text{NC,ClRuC} \rightarrow \text{I}_2$	1.653(3) [1.643(3)]	2.249(3)	2.8968(3)	5.146
$\text{OCN,ClRuC} \rightarrow \text{I}_2$	1.649(6) [1.641(2)]	2.250(6)	2.9020(6)	5.153
$\text{Br,ClRuC} \rightarrow \text{I}_2$	1.655(7) [1.640(2)]	2.235(7)	2.9115(7)	5.146
$\text{Cl}_2\text{RuC} \rightarrow \text{I}_2$	1.655(3) [1.632(6)]	2.233(3)	2.9172(4)	5.150
$\text{I,ClRuC} \rightarrow \text{I}_2$	1.654(3) [1.644(2)]	2.227(3)	2.9246(4)	5.151
$\text{OCN,ClRuC} \rightarrow \text{I}_2 \rightarrow \text{I}_2$	1.659(6) [1.641(2)]	2.104(6)	3.0536(6)	5.148

[a] Ru–C distance from the corresponding parent terminal carbide complex in brackets.

shows significant elongations (0.146–0.339 Å, 5.4–12.5 % compared to free I_2 with 2.715(6) Å^[15]), which testifies to σ -donation from the carbide lone pair into the σ^* orbital of I_2 .

The observed variation of the iodine–iodine distance (Table 1) suggests substitution of the peripheral ligands to alter the donor strength of the carbide ligands. As expected, the ability of cyanate, and in particular cyanide, to withdraw electron density by resonance reduces the σ -donor strength of their respective X_2RuC complexes, resulting in relatively short I–I bonds. The effect scales with the number of pseudohalide ligands as the dicyano complex exhibits the shortest I–I bond among the charge-transfer complexes. On the other hand, the weakly electron-withdrawing iodide provides the longest I–I distance among the all-halide $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes. Hence, the variation in the I–I distance reflects the tendency of the X ligand to withdraw electron density inductively and by resonance.

In the UV/Vis spectra, the donor–acceptor transition overlaps with transitions of the precursors (Figure S11), but Raman spectroscopy offers a complementary technique for examining the donor–acceptor interactions in the $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes. Isotopic labeling of the carbide ligands in (NC) $_2\text{RuC} \rightarrow \text{I}_2$, where ^{13}C replaces ^{12}C , shifts the band at 1036 cm^{-1} to 1000 cm^{-1} , identifying it as a $\text{Ru} \equiv \text{C}$ stretching mode. Conversely, there is no apparent shift in the intense I–I stretching frequency (at 135 cm^{-1} for both isotopes). The $\text{Ru} \equiv \text{C}$ stretching modes (1032–1036 cm^{-1}) are insensitive to the identity of X but occur at lower frequencies than those in the parent X_2RuC complexes (Cl_2RuC : 1050 cm^{-1}),^[4a] in line with weakening of the $\text{Ru} \equiv \text{C}$ bond upon coordination.

The I–I modes (115–135 cm^{-1} , Table 2) in the $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes occur at significantly lower frequencies than that of solid iodine (180 cm^{-1})^[16] and offer a quantification of the σ -donor strength of the carbide ligand. The all-halide $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes exhibit the lowest stretching frequencies with I,ClRuC inducing the largest redshift, suggesting it to be the strongest σ -donor ligand. NC,ClRuC and OCN,ClRuC induce intermediate stretching frequencies, whereas (NC) $_2\text{RuC}$

Table 2: Raman stretching frequencies [cm^{-1}] of $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes.

Complex	$\tilde{\nu}_{\text{I}-\text{I}}$	$\tilde{\nu}_{\text{Ru}=\text{C}}$	Complex	$\tilde{\nu}_{\text{I}-\text{I}}$	$\tilde{\nu}_{\text{Ru}=\text{C}}$
(NC) $_2\text{Ru}^{12}\text{C} \rightarrow \text{I}_2$	135	1036	$\text{Br,ClRuC} \rightarrow \text{I}_2$	116	1035
(NC) $_2\text{Ru}^{13}\text{C} \rightarrow \text{I}_2$	135	1000	$\text{Cl}_2\text{RuC} \rightarrow \text{I}_2$	116	1035
$\text{NC,ClRuC} \rightarrow \text{I}_2$	119	1032	$\text{I,ClRuC} \rightarrow \text{I}_2$	115	1036
$\text{OCN,ClRuC} \rightarrow \text{I}_2$	119	1035			

induces the highest stretching frequency. These findings parallel the ranking of the σ -donor strength inferred from the variation in the I–I distance. Similarly, Deplano and co-workers found Raman stretching frequencies to decrease linearly with the I–I distance in thione–iodine charge-transfer complexes ($\text{R}_2\text{C}=\text{S} \rightarrow \text{I}_2$), reflecting the thione σ -donor strength.^[17] The $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes fit surprisingly well as an extrapolation of these data (Figure 2). Thus, the X_2RuC

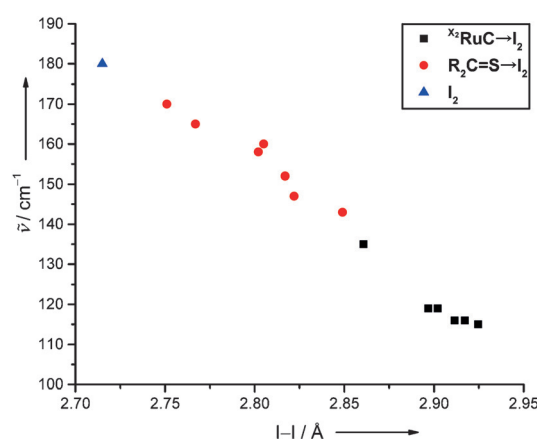


Figure 2. I–I Raman stretching frequency as a function of the I–I distance in $\text{X}_2\text{RuC} \rightarrow \text{I}_2$ complexes, $\text{R}_2\text{C}=\text{S} \rightarrow \text{I}_2$ complexes, and solid I_2 .

complexes act as stronger σ -donor ligands than thiones, and the relationship in Figure 2 represents a property of iodine which transfers well between different classes of donor molecules. Hence, the data demonstrate the ligand sphere to tune the σ -donor strength of terminal carbide ligands.

The molecular structures of the charge-transfer complexes suggest a model for the early stages of the oxidation of the carbide ligand by iodine: as the σ -donor strength of the carbide ligand increases, its separation from the outermost iodine atom remains nearly constant, while the innermost iodine atom approaches in an incipient atom transfer forming an iodicarbene and iodide.

Reaction of OCN,ClRuC with excess iodine produces $\text{OCN,ClRuC} \rightarrow \text{I}_2$ and small amounts of $[(\text{Cy}_3\text{P})_2(\text{OCN})\text{ClRu} \equiv \text{C} \rightarrow \text{I}-\text{I} \rightarrow \text{I}-\text{I}]$ ($\text{OCN,ClRuC} \rightarrow \text{I}_2 \rightarrow \text{I}_2$, Scheme 1 and Figure 3). This twofold charge-transfer complex shows a second iodine molecule to attach to the outermost iodine atom of formal $\text{OCN,ClRuC} \rightarrow \text{I}_2$. Here, the distance between I1 and I2 well surpasses the I–I distances in the remaining charge-transfer complexes (see Table 1), whereas the distance between C1 and I1 is comparatively short (2.104(6) Å) and similar to the C–I distance in methyl iodide (2.13(6) Å).^[18] This suggests the

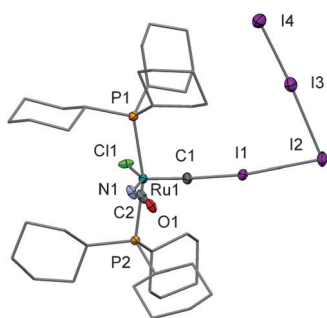
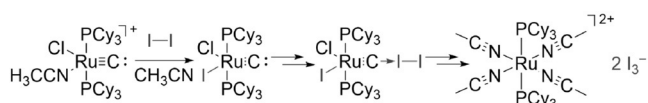


Figure 3. Molecular structure of $[\text{OCN,Cl}]\text{RuC} \rightarrow \text{I}_2 \rightarrow \text{I}_2$. Thermal ellipsoids correspond to the 50% probability level. H atoms are omitted, and cyclohexyl groups are shown as wireframe.

second I_2 molecule to assist in abstracting iodide as I_3^- , a situation that represents a conceivable forerunner of the unobserved iodocarbene triiodide salt.^[8] Fully developed triiodide ions also result from the extended reaction between I_2 and $[(\text{Cy}_3\text{P})_2\text{Cl}(\text{CH}_3\text{CN})\text{Ru}=\text{C}]^+$ to yield, inter alia, *trans*- $[(\text{Cy}_3\text{P})_2(\text{CH}_3\text{CN})_4\text{Ru}](\text{I}_3)_2$ (Scheme 2 and the Supporting Information), where the carbide ligand is abstracted from the ruthenium center. In parallel, the ligand-exchange products, $^{\text{I,Cl}}\text{RuC}$ and $^{\text{I,Cl}}\text{RuC} \rightarrow \text{I}_2$, also result from this reaction. Overall, the oxidation of the carbide ligand can be envisaged to proceed through coordination of I_2 followed by electron transfer and association with another I_2 molecule, generating triiodide and an iodocarbene.



Scheme 2. Reaction between I_2 and $[(\text{Cy}_3\text{P})_2\text{Cl}(\text{CH}_3\text{CN})\text{Ru}]^+$.

The terminal ruthenium carbide complexes $[(\text{Cy}_3\text{P})_2\text{X}_2\text{Ru}=\text{C}]$, X = halide or pseudohalide, resist oxidation in reactions with iodine, forming a suite of charge-transfer complexes $[(\text{Cy}_3\text{P})_2\text{X}_2\text{Ru}=\text{C} \rightarrow \text{I}-\text{I}]$. The X ligands induce a range of I–I bond elongations and Raman vibrational redshifts as a carry-over from variations of the carbide σ -donor strength. Iodine's role as reporter molecule could potentially be expanded to probe bonding in its (yet unknown) complexes with multiply bonded ligands such as nitride or oxide. In addition, tuning of the chemical properties of terminal carbide ligands represents an appealing parallel of the use of nitride in bond-forming and atom-transferring reactions.^[19]

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Keywords: carbide ligands · charge transfer · coordination-sphere design · iodine · ruthenium

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