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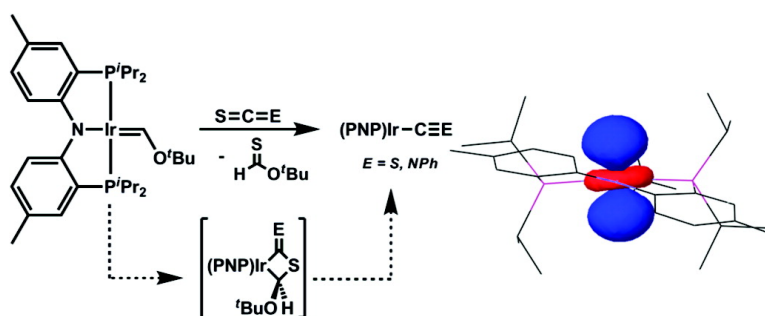
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Elucidation of Heterocumulene Activation by a Nucleophilic-at-Metal Iridium(I) Carbene

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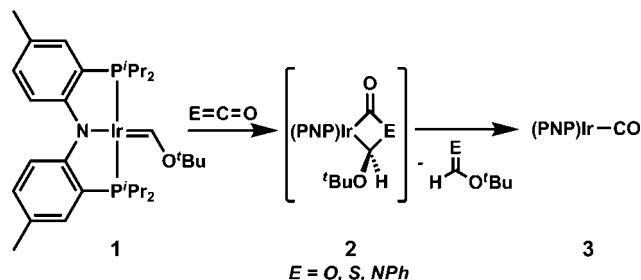
A carbene complex supported by the (PNP)Ir framework is shown to facilitate sulfur-atom transfer from CS₂ and PhNCS by an unusual multiple-bond metathesis pathway, and kinetically trapped intermediates are provided to support the proposed metal-initiated mechanism for heterocumulene activation. Experimental and theoretical studies on a series of (PNP)Ir–L complexes suggest that a high-lying, nucleophilic Ir(d₂) orbital mediates this unique reactivity. The combination of evidence indicates that square-planar Ir(I) carbenes of this type are best formulated as nucleophilic-at-metal carbenes, exhibiting reactivity initiated by a nucleophilic metal center rather than a nucleophilic or electrophilic carbene and providing products that are complementary to those typically observed for high-valent alkylidenes.

Introduction

The reactivity of transition metal–carbon multiple bonds has been the subject of intense investigation for many years, allowing the development of a host of transformations based on reactivity of the carbene unit.¹ In general, these transformations are dominated by carbon-based frontier orbitals.² Thus, metal–carbon multiple bonds are conventionally divided into two classes, where Fischer carbenes (coordinated singlet carbenes) are electrophilic at carbon and Schrock carbenes (coordinated triplet carbenes) are nucleophilic at carbon.

We have been investigating the reactivity of iridium species supported by Ozerov's PNP ligand (PNP = [N(2-P'Pr₂-4-Me-C₆H₃)₂][−])³ and recently reported an unusual transformation of carbon dioxide, carbonyl sulfide, and phenyl isocyanate, where atom and group transfer to a Fischer carbene at square-planar iridium(I) was effected by C=E bond cleavage (E = O, S, NPh).⁴ We proposed that these unique metathesis reactions were

Scheme 1. Decarbonylation of Heterocumulenes by Carbene 1



made possible by a nucleophilic iridium center, which could initiate atom and group transfer by attack of an electrophilic heterocumulene, cyclization to metallacycle **2**, and elimination of formate, thioformate, or formimidate to afford (PNP)Ir–CO (**3**, Scheme 1).

This formulation implies that the high d-electron count and coordinatively unsaturated nature of carbene **1** confer a degree of nucleophilicity to the iridium center that controls reactivity of the complex, contrasting previous reports of heterocumulene reactivity where the metal-bound carbenes act as nucleophiles and C–C bonds are formed.^{5,6} Such behavior would not be entirely unexpected in light of Roper's previous observation, which we have confirmed for our system,⁴ that heteroatom-substituted carbenes rarely exhibit electrophilic character when attached to electron-rich, late transition metals.^{2f} Additionally, Stone has reported that a square-planar carbene of iridium(I) performs the oxidative addition of dihydrogen, affording an

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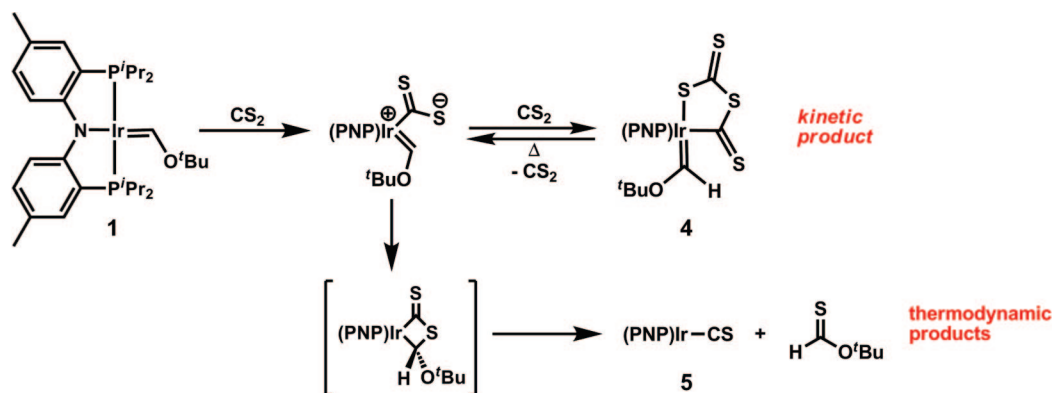
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Scheme 2. Reaction of Carbene **1** with Carbon Disulfide

iridium(III) dihydrido carbene.⁷ By analogy, the electron-rich metal center in our system might be expected to play a central role in substrate activation.

In this contribution, we report that reaction of **1** with CS_2 and PhNCS , which are isoelectronic to the heterocumulenes previously examined, allows observation and isolation of kinetically trapped intermediate species, supporting a mechanism of atom transfer that clearly requires a distinct mode of carbene reactivity. Additionally, we present experimental and theoretical studies suggesting that a high-lying, nucleophilic $\text{Ir}(\text{d}_z^2)$ orbital plays a critical role in initiating these unusual transformations. Taken together, our findings suggest a new strategy for the activation of heterocumulenes and other electrophiles across metal–ligand multiple bonds at late transition metals. Interestingly, these reactivity patterns are complementary to those observed for the nucleophilic alkylidenes of the high-valent early metals.^{2a,5a,8}

Results and Discussion

I. Reactivity with Carbon Disulfide. In light of the high driving force for the formation of carbonyl complex **3**, reaction of carbene **1** with heterocumulenes lacking oxygen was examined with the goal of stabilizing an intermediate species analogous to metallacycle **2**. However, in contrast to the reactivity observed with oxygen-containing heterocumulenes,⁴ dissolution of $(\text{PNP})\text{Ir}=\text{C}(\text{H})\text{O}^t\text{Bu}$ (**1**) in neat CS_2 did not afford $(\text{PNP})\text{Ir}-\text{CS}$ but instead yielded the unusual CS_2 head-to-tail dimer complex **4**, in which the iridium carbene unit remained intact (Scheme 2),^{9,10} as confirmed by X-ray diffraction analysis (Figure 1). The carbene proton retains a distinctive ^1H NMR shift (δ 15.5 ppm), consistent with an iridium–carbon multiple bond, but collapses from a triplet (in complex **1**) to a singlet (in complex **4**) due to the shifting of the C–H bond vector out

of the plane of the iridium–phosphorus bonds.¹¹ The carbene is observed by ^{13}C NMR at δ 266.7 ppm, shifted significantly downfield from the parent *tert*-butoxymethylidene (δ 210.0 ppm).¹² As a result of the change in metal oxidation state, the $\text{Ir}=\text{C}$ bond of **4** is slightly elongated (1.96 Å) relative to compound **1** (1.88 Å), and the $\text{C}(27)-\text{O}(1)$ bond is contracted by approximately the same amount (from 1.35 Å to 1.28 Å), indicating a decrease in metal–carbon multiple-bond character and concomitant increase in the effective carbon–oxygen bond order.

Heating a benzene solution of **4** (70 °C, 16 h) caused quantitative degradation to $(\text{PNP})\text{Ir}-\text{CS}$ (**5**) with concomitant expulsion of *tert*-butyl thioformate and CS_2 (Scheme 2), indicating the potential intermediacy of CS_2 dimer **4** in the sulfur-atom transfer process (and suggesting CO_2 dimers as possible intermediates in previously reported oxygen-atom transfer reactions).¹⁰ However, previous studies of the kinetics of CO_2 deoxygenation by **1** had shown a first-order rate dependence on CO_2 concentration, indicating that such a mechanism was not operative.⁴ Additionally, the connectivity of **4** is more consistent with intermediates typically invoked in heterocumulene disproportionation reactions.¹³ Thus, we were interested to see whether **4** was instead a kinetic product formed from the trapping of an intermediate species formed by reaction of **1** with CS_2 .

Slow addition of 1 equiv of CS_2 to a benzene solution of **1** resulted in the immediate and quantitative formation of thio-carbonyl complex **5** at *ambient temperature*, ruling out the intermediacy of **4** in the atom transfer reaction. Thus, as in our original assessment of the mechanism, we propose that reaction begins with nucleophilic attack by iridium at an electrophilic heterocumulene carbon. Depending on the concentration of CS_2 , two pathways are available for this intermediate, and it can either be trapped by a second molecule of CS_2 , affording **4**, or cyclize to the irida(dithio)lactone and decompose to give **5** and *tert*-

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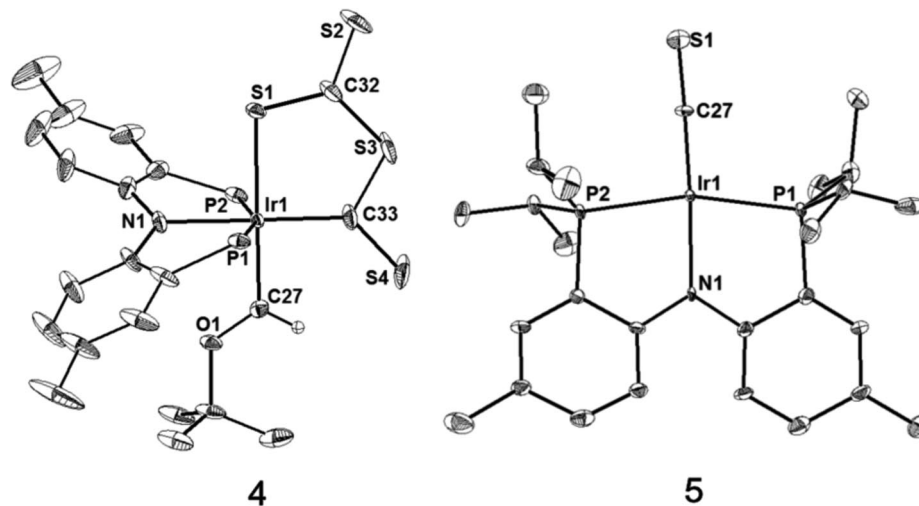


Figure 1. Displacement ellipsoid (30%) representation of complexes **4** (left) and **5** (right) with ^tPr phosphine substituents omitted from **4** for clarity. Relevant bond lengths (Å) and angles (deg), for **4**: Ir1–C27 1.960(4), Ir1–S1 2.397(1), Ir1–N1 2.119(4), Ir1–C33 1.998(5), Ir1–P1 2.350(1), Ir1–P2 2.357(1), C27–O1 1.281(5), S1–Ir1–C27 179.1(1), N1–Ir1–C33 178.5(2), P1–Ir1–P2 159.52(4). For **5**: Ir1–C27 1.82(2), Ir1–N1 2.04(1), Ir1–P1 2.298(3), Ir1–P2 2.290(3), N1–Ir1–C27 170.0(7), P1–Ir1–P2 164.2(1).

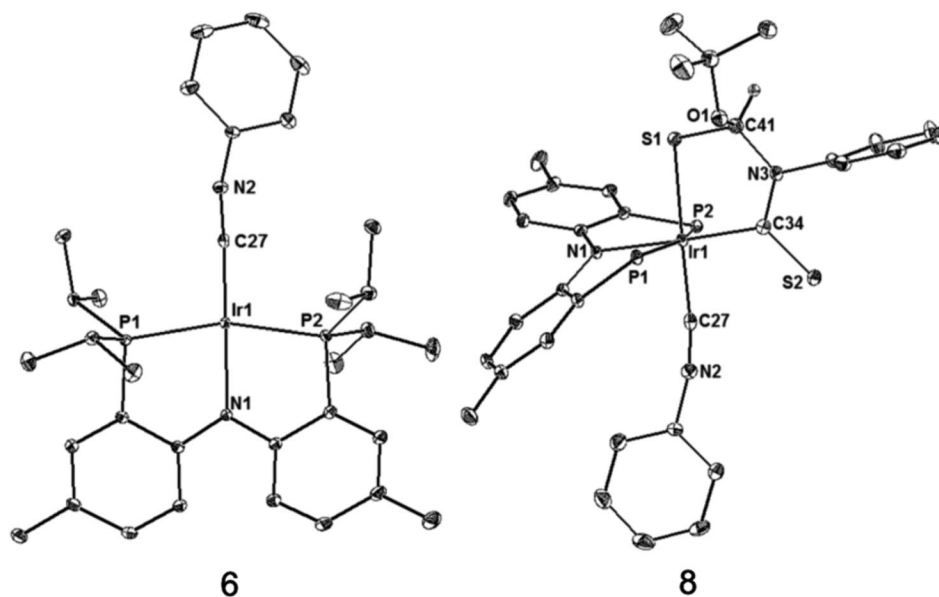


Figure 2. Displacement ellipsoid (30%) representation of complexes **6** (left) and **8** (right) with ^tPr phosphine substituents omitted from **8** for clarity. Relevant bond lengths (Å) and angles (deg), for **6**: Ir1–C27 1.852(1), Ir1–N1 2.071(9), Ir1–P1 2.2811(3), Ir1–P2 2.2877(3), C27–N2 1.197(1), N1–Ir1–C27 177.09(4), P1–Ir1–P2 162.16(1). For **8**: Ir1–C27 1.937(2), Ir1–S1 2.3648(5), Ir1–N1 2.155(2), Ir1–C34 2.049(2), Ir1–P1 2.3392(6), Ir1–P2 2.3533(6), C27–Ir1–S1 177.47(6), N1–Ir1–C34 177.42(6), P1–Ir1–P2 160.36(2).

butylthioformate as thermodynamic products (Scheme 2).¹⁴ Therefore, compound **4** can be viewed as a protected form of an intermediate species in the atom transfer reaction, supporting the view that atom and group transfers to carbene complex **1** are initiated by a nucleophilic metal rather than an electrophilic carbene ligand.^{15,16} This interpretation is also consistent with

(14) It is possible that the CS₂ adduct and dithiolactone shown in Scheme 2 are in equilibrium, but we currently have no evidence supporting this view.

(15) The reactivity of metal–ligand multiple bonds with carbon disulfide is typically initiated by nucleophilic ligands: (a) Mayr, A.; Lee, T.-Y. *Angew. Chem., Int. Ed.* **1993**, 32, 1726. (b) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, 19, 4795.

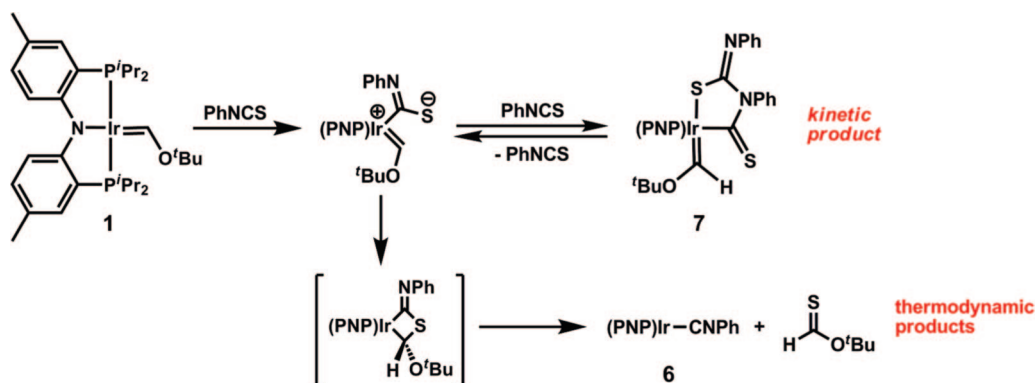
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the observation that reductive condensations of CS₂ are generally promoted by nucleophilic, electron-rich metal centers.^{9a,e}

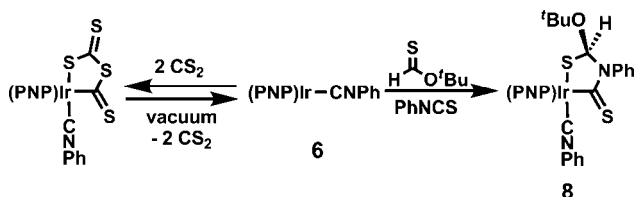
II. Reaction with Phenyl Isothiocyanate. The reactivity of **1** with isothiocyanates is considerably more complex, and depending on reaction conditions, several species were observed to form. In analogy to reaction with CS₂, slow addition of **1** equiv of PhNCS to a dilute solution of Fischer carbene **1** resulted in quantitative sulfur-atom transfer to generate (PNP)Ir–CNPh (**6**, Figure 2) and *tert*-butyl thioformate (Scheme 3). Although metal-mediated desulfurization of isothiocyanates has been reported,^{16b,17} this process typically occurs by sulfur-atom transfer to a phosphine ligand and has not been observed for metal-bound carbenes.

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Scheme 3. Reaction of Carbene 1 with Phenyl Isothiocyanate



Scheme 4. Nucleophilic Reactivity of Isocyanide Complex 6



In light of the reactivity observed for CS_2 , we were hopeful that exposure of **1** to an excess of PhNCS would allow the isolation of an iridium-supported PhNCS dimer similar to **4**. Addition of an excess (2–10 equiv) of PhNCS to concentrated solutions of **1** led to the formation of species **7**, for which the spectroscopic data proved nearly identical to those of CS_2 dimer **4**, particularly the distinctive shift of the carbene proton in ^1H NMR (δ 15.5 ppm). However, this apparent PhNCS dimer was observed to decompose quickly (1 h) to isocyanide complex **6**, indicating the more facile reversibility of PhNCS versus CS_2 condensation in these complexes.

In the presence of excess PhNCS and *tert*-butyl thioformate, compound **6** converts to a new, structurally unusual species **8**, in which the C_s symmetry has been broken (Scheme 4). X-ray diffraction analysis of single crystals of **8** revealed the structural motif depicted in Figure 2, which results from the reductive condensation of PhNCS and *tert*-butyl thioformate. Based on the structure observed for complex **8** and the spectroscopic similarities between complexes **7** and **4**, we tentatively assign the connectivity of the unstable PhNCS dimer **7** as shown in Scheme 3. Although the isomeric metallacycle resulting from C–S bond formation is the more commonly observed product of isothiocyanate condensation (I in Figure 3),^{9e,13d} metallacycles such as **7**, which result from C–N bond formation, have been reported (II in Figure 3).^{13e,18}

Isocyanide complex **6** was also shown to react with large excesses of CS_2 , forming varying amounts of a species formulated as the $\text{C}_2\text{S}_4^{2-}$ adduct of the isocyanide complex analogous to CS_2 dimer **4** (observed by ^1H and ^{31}P NMR). Unlike **4**, which is stable in solution and the solid state at ambient temperature, this adduct is in equilibrium with isocya-

nide complex **6**, and application of vacuum causes quantitative regeneration of **6** (Scheme 4). Nevertheless, the analogies between the nucleophilic reactivity observed for $(\text{PNP})\text{Ir}-\text{CNPh}$ (**6**) and $(\text{PNP})\text{Ir}=\text{C}(\text{H})\text{O}^t\text{Bu}$ (**1**) highlight the isoelectronic relationship between these molecules and suggest that computational studies can illuminate the factors controlling reactivity of these types of molecules.

III. Computational Examination of $(\text{PNP})\text{Ir}-\text{L}$ Complexes. Having obtained experimental support for our proposed mechanism of nucleophilic attack by iridium to initiate atom and group transfer reactions from heterocumulenes, we turned our attention to computational methods to help elucidate the ground-state configuration of the carbene shown to effect these unusual transformations. Using the atomic coordinates determined from the crystal structure of **1**, density functional calculations were performed at the B3LYP/LACVP** level of theory. The molecular surfaces of the frontier orbitals produced by these calculations are represented in Figure 4 (HOMO–1, HOMO, and LUMO).

As predicted from simple molecular orbital considerations, the frontier orbitals represent the nonbonding $\text{Ir}(d_{z^2})$, iridium–carbene π , and iridium–carbene π^* orbitals. In contrast to the HOMO and LUMO, which are significantly delocalized over the molecule, the HOMO–1 is localized entirely on iridium, representing a prototypical d_{z^2} orbital. Based on the reactivity patterns observed previously and in this report, we propose that this high-lying, localized orbital is primarily responsible for the nucleophilic activation of heterocumulene substrates, leading to group transfer or reductive condensation.

Since $(\text{PNP})\text{Ir}=\text{C}(\text{H})\text{O}^t\text{Bu}$ (**1**), $(\text{PNP})\text{Ir}-\text{CO}$ (**3**), $(\text{PNP})\text{Ir}-\text{CS}$ (**5**), and $(\text{PNP})\text{Ir}-\text{CNPh}$ (**6**) are isoelectronic, DFT calculations were extended to this entire series of molecules.¹⁹ In fact, the gross ordering and shape of the orbitals remain constant throughout the series. However, the energies of the high-lying orbitals, particularly d_{z^2} (HOMO–1), vary across the series, reflecting to some degree the relative reactivities of the molecules.

As described above, carbene complex **1**, for which the HOMO–1 orbital is highest in energy (Table 1), forms the dimeric adduct **4** upon reaction with excess CS_2 . Isocyanide complex **6**, which possesses a d_{z^2} orbital close in energy to that calculated for **1**, reacts with CS_2 to generate the analogous dimeric adduct (Scheme 4). The carbonyl and thiocarbonyl complexes, which have significantly lower energy calculated d_{z^2} orbitals (Table 1), show no evidence for reactivity with neat

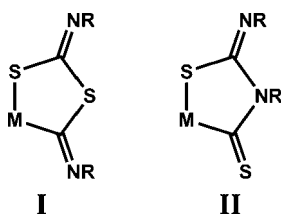


Figure 3. Common bonding motifs for isothiocyanate dimers.

(18) Itoh, K.; Matsuda, I.; Ueda, F.; Ishii, Y.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2118.

(19) Further details regarding calculations on **1**, **3**, **5**, and **6** are provided in the Supporting Information.

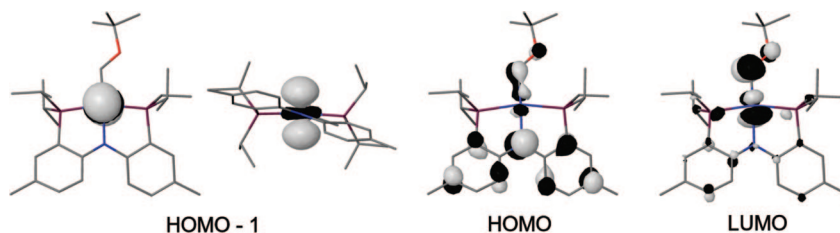


Figure 4. Molecular surfaces of frontier orbitals calculated for (PNP)Ir=C(H)O'Bu (**1**).

Table 1. Energies of Ir(d_z^2) Orbitals for (PNP)Ir–L Molecules

complex	energy of HOMO–1 (eV)
(PNP)Ir=C(H)O'Bu (1)	–4.62
(PNP)Ir–CNPh (6)	–4.80
(PNP)Ir–CO (3)	–4.99
(PNP)Ir–CS (5)	–5.22

CS₂ or PhNCS. Thus, as outlined in Table 1, the propensity of a (PNP)Ir–L complex to form a C₂S₄^{2–} adduct with CS₂ is correlated to the relative destabilization of the d_z^2 molecular orbital (HOMO–1), consistent with our proposed mechanism.

Conclusions

In conclusion, we have reported well-defined sulfur-atom transfer reactions from CS₂ and PhNCS to an iridium-supported Fischer carbene. These reactions represent, to the best of our knowledge, the first examples of sulfur-atom transfer from heterocumulenes across an M=C bond and appear to be facilitated by the nucleophilic character of the iridium center of complex **1**. Under suitable conditions, exposure of carbene **1** to these reagents allows observation of trapped kinetic adducts, which clearly require a metal-initiated mechanism, in contrast to the standard reactivity patterns observed for metal carbenes.² DFT calculations were performed on a series of (PNP)Ir–L molecules and highlight the importance of a high-lying, nucleophilic Ir(d_z^2) orbital in initiating this unusual heterocumulene reactivity.

Drawing from these experimental and theoretical results, we propose that complex **1** is best formulated as a nucleophilic-at-metal carbene. It is particularly beneficial to consider these findings in relation to the known reactivity of high-valent alkylidene complexes of the early metals. Schrock has reported that a tris(neopentyl)neopentylidene tantalum(V) complex reacts instantaneously with CO₂ to produce di-*tert*-butylallene and a polymeric tantalum oxide (Scheme 5)^{5a} and has proposed that this and related olefination reactions proceed by initial substrate coordination to the coordinatively unsaturated, highly electrophilic tantalum.²⁰ Subsequent group transfer releases olefin and attaches the strongly π -basic oxo ligand to the high-valent tantalum center. In contrast, we have reported that the square-planar iridium(I) carbene **1** attacks the electrophilic central

carbon of CO₂,⁴ ultimately oxygenating the carbene ligand and transferring a strongly π -acidic carbonyl to the electron-rich, d⁸ iridium center, providing a complementary reactivity pathway to the tantalum case (Scheme 5).

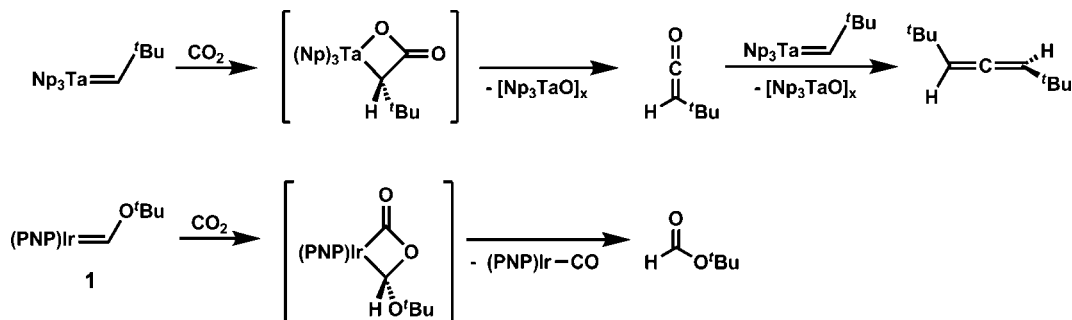
The carbene ligand of **1** ultimately acts as an electrophile in the reported reactions, consistent with the classical behavior of Fischer-type carbenes, but this only occurs after substrate activation by the electron-rich iridium center renders the heterocumulene more nucleophilic and the carbene more electrophilic. Thus, the coordinatively unsaturated nature of the carbene complex reveals a distinct pathway for the activation of multiple bonds via a metal- rather than ligand-initiated mechanism. These findings suggest that square-planar carbenes of the late transition metals may generally exhibit a strong propensity to activate electrophilic substrates toward atom and group transfer across metal–carbon multiple bonds, and the application of these types of transformations in catalytic processes is the subject of ongoing investigation.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with Ar gas followed by passage through an activated alumina column.²¹ (PNP)Ir=C(H)O'Bu (**1**) and (PNP)Ir–CO (**3**) were prepared according to literature procedure.⁴ Phenyl isothiocyanate was purchased from Aldrich and degassed in vacuo prior to use. Other reagents were purchased from commercial vendors and used without further purification. Elemental analyses were carried out at Desert Analytics, Tucson, AZ. NMR spectra were recorded at ambient temperature on Varian Mercury 300 and 500 MHz spectrometers. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent. ³¹P NMR chemical shifts are reported relative to an external standard of 85% H₃PO₄. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker KAPPA APEX II diffractometer.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard

Scheme 5. Contrasting CO₂ Reactivity of Schrock-Type and Nucleophilic-at-Metal Carbenes (Np = neopentyl)



Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure.

Computational Methods. Hybrid density functional theory calculations were performed for (PNP)Ir=C(H)O'Bu (**1**), (PNP)Ir-CO (**3**), (PNP)Ir-CS (**5**), and (PNP)Ir-CNPh (**6**) using the Jaguar package (version 7.5, release 110), employing the B3LYP functional and 6-31G** basis set.²² Iridium was represented with the LACVP** basis set.^{23,24} Atomic coordinates were imported from relevant single-crystal X-ray structures and subjected to geometry optimization.

Preparation of (PNP)Ir=C(H)O'Bu(C₂S₄) (4**).** To a stirring solution of (PNP)Ir=C(H)O'Bu (**1**) (50.0 mg, 0.0707 mmol) in pentane (5 mL) was added excess carbon disulfide (ca. 200 μ L), causing the immediate precipitation of a brown-orange solid. The solution was stirred for 15 min and the orange powder isolated by filtration. The powder was dissolved in a minimal amount of THF, and analytically pure red crystals of **4** were isolated by vapor diffusion of pentane into the concentrated THF solution (28.0 mg, 46%). ¹H NMR (C₆D₆): δ 15.55 (s, 1H, -C(H)O'Bu), 7.53 (dt, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 2H, Ar-H), 6.73 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 2H, Ar-H), 6.58 (m, 2H, Ar-H), 2.74 (m, 2H, -CH(CH₃)₂), 2.11 (s, 6H, Ar-CH₃), 2.09 (m, 2H, -CH(CH₃)₂), 1.11 (m, 12H, -CH(CH₃)₂), 0.91 (dvt, 6H, -CH(CH₃)₂), 0.77 (s, 9H, -C(CH₃)₃), 0.74 (dvt, 6H, -CH(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 269.7 (Ir-CS₂), 266.7 (Ir-C(H)O'Bu), 236.8 (Ir-SCS₂). ³¹P{¹H} NMR (C₆D₆): δ 20.5 (s). Anal. Calcd for C₃₃H₅₀IrNOP₂S₄: C, 46.13; H, 5.87; N, 1.63. Found: C, 45.98; H, 5.81; N, 1.57.

Preparation of (PNP)Ir-CS (5**).** **Method A.** A resealable NMR tube was charged with compound **4** (24.0 mg, 0.0279 mmol) in THF (ca. 1 mL) and heated at 70 °C for 16 h, causing a slight lightening of the solution from brownish-red to pale red. NMR spectroscopy confirmed the presence of **5** as the sole component.

Method B. Compound **1** (31.1 mg, 0.0440 mmol) was dissolved in benzene (3 mL) and carbon disulfide (2.7 μ L, 0.045 mmol) added dropwise as a dilute solution in benzene (1 mL), causing a color change from purple to pale red. After 30 min, volatile components were removed in vacuo and the residues were crystallized by slow evaporation of pentane from a concentrated solution to afford brown-red crystals of analytically pure **5** (25.4 mg, 87%). ¹H NMR (C₆D₆): δ 7.58 (d, J = 8.4 Hz, 2H, Ar-H), 6.96 (br s, 2H, Ar-H), 6.78 (d, J = 8.7 Hz, 2H, Ar-H), 2.55 (m, 4H, -CH(CH₃)₂), 2.17 (s, 6H, Ar-CH₃), 1.42 (dvt, 12H, -CH(CH₃)₂), 1.15 (dvt, 12H, -CH(CH₃)₂). ¹³C{¹H} NMR (C₆D₆): δ 262.0 (Ir-CS). ³¹P{¹H} NMR (C₆D₆): δ 53.2 (s). Anal. Calcd for C₂₇H₄₀IrNP₂S: C, 48.78; H, 6.06; N, 2.11. Found: C, 48.52; H, 6.06; N, 2.03.

Preparation of (PNP)Ir-CNPh (6**).** Phenyl isothiocyanate (9.15 μ L, 0.0765 mmol) was added dropwise as a solution in benzene (1 mL) over 1 min to a stirring purple solution of compound **1** in benzene (5 mL), causing a gradual color change to red-orange over a period of 30 min. Volatiles were removed in vacuo to afford an orange powder, which was crystallized by slow evaporation of pentane from a concentrated solution to afford analytically pure **6** as orange crystals (40.0 mg, 72%). ¹H NMR (C₆D₆): δ 7.79 (d, J = 8.7 Hz, 2H, Ar-H), 7.33 (d, J = 7.5 Hz, 2H, Ar-H), 7.10–6.90 (m, 5H, Ar-H), 6.85 (d, J = 8.1 Hz, 2H, Ar-H), 2.38 (septet, ³J_{HH} = 3.0 Hz, -CH(CH₃)₂), 2.22 (s, 6H, Ar-CH₃), 1.35 (dvt, 12H, -CH(CH₃)₂), 1.14 (dvt, 12H, -CH(CH₃)₂). ¹³C{¹H} NMR (C₆D₆): δ 176.8 (t, ³J_{PC} = 9.3 Hz, Ir-CNPh). ³¹P{¹H} NMR (C₆D₆): δ 53.6

(s). Anal. Calcd for C₃₃H₄₅IrN₂P₂: C, 54.75; H, 6.27; N, 3.87. Found: C, 54.87; H, 6.20; N, 3.86.

Observation of Complex 7. Phenyl isothiocyanate (9.1 μ L, 0.076 mmol) was added in one portion to an NMR tube containing a solution of complex **1** (24.4 mg, 0.0345 mmol) in C₆D₆ (600 μ L), causing an immediate color change from dark purple to bright red. After 15 min, analysis of the solution by NMR revealed a mixture of complexes **7** and **1** (70:30). Spectral data for complex **7**: ¹H NMR (C₆D₆): δ 15.5 (s, 1H, Ir=C(H)O'Bu), 7.59 (d, J = 8.4 Hz, 2H, Ar-H), 7.53–7.35 (m, 4H, Ar-H), 7.29–7.19 (m, 4H, Ar-H), 6.81–6.63 (m, 6H, Ar-H), 3.01 (m, 2H, -CH(CH₃)₂), 2.19 (m, 2H, -CH(CH₃)₂), 2.13 (s, 6H, Ar-CH₃), 1.47–1.29 (m, 12H, -CH(CH₃)₂), 1.19 (dvt, 6H, -CH(CH₃)₂), 1.00 (dvt, 6H, -CH(CH₃)₂). ³¹P{¹H} NMR (C₆D₆): δ 18.8 (br s).

Preparation of Complex 8. Phenyl isothiocyanate (8.2 μ L, 0.069 mmol) was added dropwise as a solution in benzene (1 mL) over 1 min to a stirring purple solution of complex **1** (48.0 mg, 0.0679 mmol) in benzene (5 mL), causing a gradual color change to red-orange over a period of 30 min. After 2 h, additional phenyl isothiocyanate (ca. 100 μ L) was added as a solution in benzene (1 mL) to the stirring reaction, causing further lightening to bright orange. After 24 h, volatiles were removed in vacuo and the residues crystallized by slow evaporation of pentane from a concentrated solution to afford complex **8** as bright orange crystals (25.4 mg, 39%). ¹H NMR (C₆D₆): δ 7.68 (d, J = 6.9 Hz, 1H, Ar-H), 7.60 (m, 1H, Ar-H), 7.52 (m, 1H, Ar-H), 7.40 (m, 1H, Ar-H), 7.31–7.16 (m, 4H, Ar-H), 7.15–6.94 (m, 3H, Ar-H), 6.92–6.69 (m, 3H, Ar-H), 6.63 (m, 2H, Ar-H), 6.24 (s, 1H, -CH(O'Bu)), 3.96 (m, 1H, -CH(CH₃)₂), 3.45 (m, 1H, -CH(CH₃)₂), 2.67 (m, 1H, -CH(CH₃)₂), 2.48 (m, 1H, -CH(CH₃)₂), 2.18 (s, 3H, Ar-CH₃), 2.16 (s, 3H, Ar-CH₃), 1.97 (m, 3H, -CH(CH₃)₂), 1.80–1.45 (m, 9H, -CH(CH₃)₂), 1.38–0.98 (m, 12H, -CH(CH₃)₂), 0.90 (s, 9H, -C(CH₃)₃). ³¹P NMR (C₆D₆): δ 16.1 (d, ²J_{PP} = 361 Hz), 7.5 (d, ²J_{PP} = 361 Hz). Anal. Calcd for C₄₅H₆₀IrN₃OP₂S₂: C, 55.31; H, 6.19; N, 4.30. Found: C, 55.12; H, 6.15; N, 4.06.

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Supporting Information Available: Calculated surfaces and energies for frontier molecular orbitals of **1**, **3**, **5**, and **6**. Crystallographic details for complexes **4**, **5**, **6**, and **8** are provided in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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