Metal Ion Mediated Transfer and Cleavage of Diaminocarbene Ligands

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Under mild conditions, reactions of $(CO)_5M=C[N(R)CH_2]_2$ [M = W, Mo, Cr; R = Et, allyl, benzyl, 4-pentenyl] with $(PhCN)_2PdCl_2$, $(PhCN)_2PtCl_2$, $[(CO)_2RhCl]_2$, $(Me_2S)AuCl$, $[(CH_3CN)_4Cu]BF_4$, and $AgBF_4$ provide the corresponding diaminocarbene complexes via carbene ligand transfer. The resulting Pd(II), Pt(II), Rh(I), and Au(I) carbene complexes are stable and were isolated. The Cu(I) and Ag(I) complexes readily undergo acid-induced M=C cleavage to yield the imidazolidin-2-ylidinium salts. The carbene-transfer reactions were studied for two phosphine donors: $(CO)_m(L)W=C[N(R)CH_2]_2$ {R = Et, benzyl; L = PPh_3, m = 4; L = dppe, m = 3}. The X-ray crystal structures of $(CO)_5W=C[N(CH_2C_6H_5)CH_2]_2$ (**1c**), *cis*-$(CO)_4$-$(PPh_3)W=C[N(CH_2C_6H_5)CH_2]_2$ (**5b**), *fac*-$(CO)_3(dppe)W=C[N(CH_2C_6H_5)CH_2]_2$ (**6b**), $Cl_2(CO)$-$Pt=C[N(CH_2C_6H_5)CH_2]_2$ (**9c**), and *cis*-$Cl_2Pt\{=C[N(CH_2C_6H_5)CH_2]_2\}_2$ (**11b**) are reported.

Introduction

Fundamental studies of synthetic approaches and properties of transition metal carbene complexes are still an interesting area of research.[1,2] Several synthetic approaches have been established for the preparation of metal carbene complexes,[3−11] but few investigations involving carbene transfer between metal ions to generate new carbene species have been reported.[4]

Diamino-substituted carbenes are unusually stable due to the good σ-donating ligand.[5−11] It occurred to us that the stable diaminocarbene makes them suitable for studying carbene transfer between metal ions. In a preliminary report, we showed that carbene complexes of Pd(II), Pt(II), Rh(I), and Au(I) were formed in high yields via the reaction of tungsten diaminocarbene complexes $[(CO)_5W=CNRCH_2CH_2NR]$ with $(PhCN)_2$-$PdCl_2$, $(PhCN)_2PtCl_2$, $[(CO)_2RhCl]_2$, and $(Me_2S)AuCl$

under mild conditions, indicating that a carbene-transfer reaction between transition metal complexes can be facile.[12] To gain insight into such carbene transfer, an investigation of the reactvities of diaminocarbene complexes **1−4** toward other transition metal ions was conducted. Herein we report the carbene

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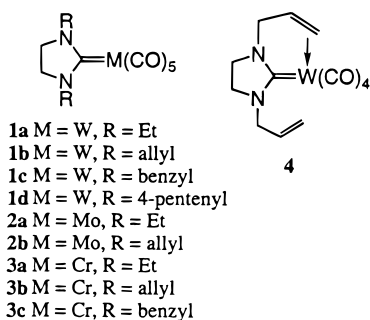‡ China Medical College.

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transfer from group VI metal carbonyl complexes to other transition metal ions and the cleavage of the $M-C_{(carbene)}$ bond by copper and silver ions.

1a M = W, R = Et
1b M = W, R = allyl
1c M = W, R = benzyl
1d M = W, R = 4-pentenyl
2a M = Mo, R = Et
2b M = Mo, R = allyl
3a M = Cr, R = Et
3b M = Cr, R = allyl
3c M = Cr, R = benzyl

Results and Discussion

Preparation of Carbene Complexes. All carbene complexes were prepared by the method previously reported for the *N*-benzyl-substituted complexes (**1c**, **2c**, and **3c**). The π-coordinated diaminocarbene complex **4** is obtained thermally by heating **1b** above 100 °C. Substitution reactions of **1a** and **1c** with triphenylphosphine or bis(diphenylphosphino)ethane (dppe) proceeded cleanly at 120 °C to produce **5a**,**b** and **6a**,**b**, respectively, in excellent yields.

All the carbene complexes were isolated as stable solids and characterized by both spectral and elemental analyses. Some spectral data are summarized in Table 1. The *facial* geometry of complexes **6** and the *cis* arrangement in **5** were established by ^{31}P NMR chemical shifts and their IR carbonyl stretching patterns. X-ray single-crystal structures of **5b** and **6b** were obtained to provide confirmation (see Crystallography section).

Carbene-Transfer Reactions. The diaminocarbene unit of group VI metal carbonyl complexes **1**–**3** is readily transferred to the other transition metal ions. We reported earlier that reaction of **1a** and **1b** with

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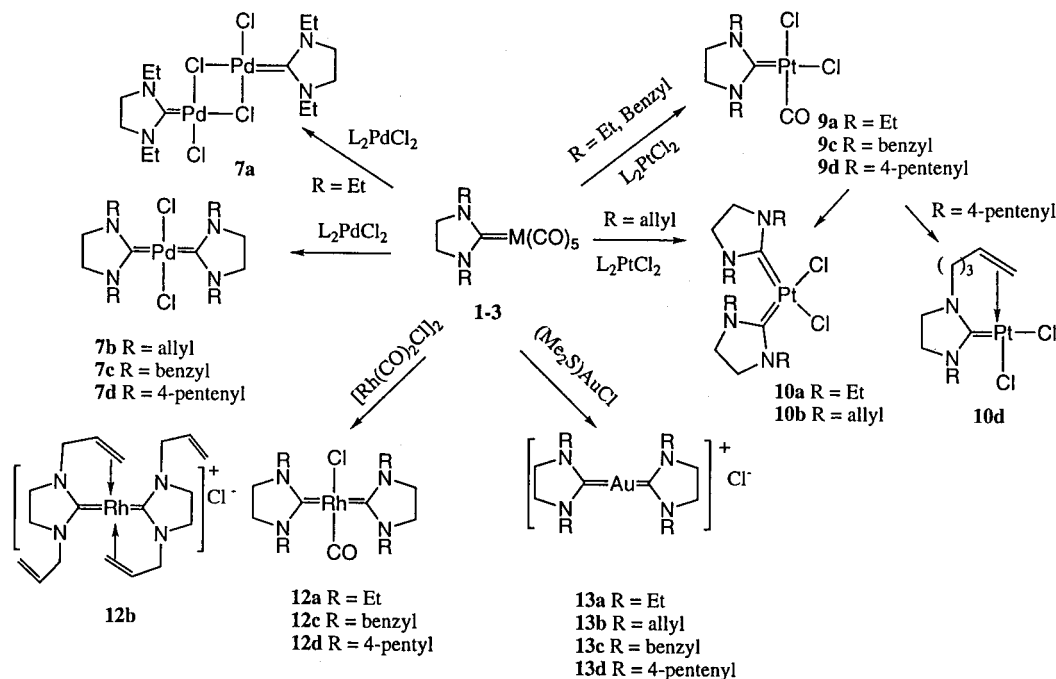
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Table 1. Some Spectral Data of Group VI Metal Carbonyl Diaminocarbenes[a]

complex	δ of carbene carbon	ν_{CO} (cm^{-1})[b]	ref
1a	205.6 (J_{W-C} = 95.7 Hz)	2062, 1919	11
1b	208.0 (J_{W-C} = 95.8 Hz)	2063, 1920	11
1c	209.1 (J_{W-C} = 95.1 Hz)	2064, 1922	this work
1d	207.2 (J_{W-C} = 96.0 Hz)	2062, 1919	this work
2a	214.1	2063, 1928	11
2b	215.9	2064, 1928	11
3a	219.2	2054, 1929	11
3b	220.6	2064, 1928	11
3c	221.6	2056, 1924	this work
4	216.8 (J_{W-C} = 91.7 Hz)	2022, 1918, 1863	11
5a	214.1 (J_{P-C} = 8.4 Hz)	2002, 1874, 1853	this work
5b	217.6 (J_{P-C} = 8.3 Hz)[c]	2004, 1876, 1854	this work
6a	210.8 (J_{P-C} = 5.9 Hz)	1919, 1820	this work
6b	210.2 (J_{P-C} = 6 Hz)[c]	1921, 1824	this work

[a] ^{13}C NMR in CDCl$_3$. [b] IR in CH$_2$Cl$_2$. [c] In CD$_3$COCD$_3$.

5a R = Et   **6a** R = Et
5b R = Benzyl   **6b** R = Benzyl
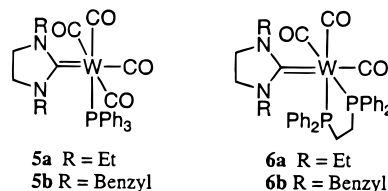
$(PhCN)_2PdCl_2$, $(PhCN)_2PtCl_2$, $[(CO)_2RhCl]_2$, and (Me_2S)-AuCl results in the formation Pd(II), Pt(II), Rh(I), and Au(I) carbene complexes, respectively, in high yields. Further investigation showed that the chromium and molybdenum diaminocarbene complexes with different *N*-substituents (**2**, **3**) behave similarly. Structural variations in the carbene transfers are summarized in Scheme 1.

Palladium–Carbene Complexes. The *N*-substituent in complexes **1a**–**1d** affects the carbene transfer dramatically with respect to both reaction rate and structure. Complex **1a** reacts with an equimolar amount of $(PhCN)_2PdCl_2$ to yield the chloro-bridged dipalladium carbene complex **7a**, whereas complexes **1b**–**d** give biscarbene palladium species upon treatment with $(C_6H_5CN)_2PdCl_2$. Reactions of **1b**–**d** leading to **7b**–**d** were complete within 0.5 h at ambient temperature, while reaction of **1a** required 2 h under refluxing conditions. These observations indicate that the π-bond functionality on the nitrogen atom accelerates the carbene transfer and influence the structure of the products.

Transformation of the carbene ligand from other group VI metal ions to palladium proceeds similarly. Thus, complexes **2a**,**b** and **3a**,**b** react with $(PhCN)_2PdCl_2$ to yield carbene complexes **7a**,**b** as the exclusive product. The ligands around the palladium metal center influence the carbene-transfer reaction; for example, none of the complexes $(CH_3CN)_2PdCl_2$, $(Ph_3P)_2PdCl_2$, $(COD)PdCl_2$, or $(COD)Pd(Me)Cl$ [COD = 1,5-cyclooctadiene] reacts with tungsten complexes to generate palladium carbenes. This result shows that a weak coordinating ligand is essential for the carbene transfer. Significantly, the π-coordinating carbene **4** does not react with $(PhCN)_2PdCl_2$, indicating that the carbene transfer is affected by the ligand surrounding the group VI metal center.

Typical ^{13}C chemical shifts of carbene–carbon in the palladium complexes are summarized in Table 2. The ^{13}C resonances of the carbene center shift upfield from

Scheme 1. Carbene Transfer between Transition Metal Ions

Table 2. ^{13}C Chemical Shifts of M=C$_{(carbene)}$ in Various Complexes^{a,b}

N-substituent	M = Pd	M = Pt	M = Rh^b	M = Au
R = Et	173.3 (**7a**)	174.3 (**10a**)	212.8 (**12a**) [36.9]	203.8 (**13a**)
R = allyl	198.7 (**7b**)	168.2 (**10b**)	202.8 (**12b**) [30.3]	205.1 (**13b**)
R = benzyl	199.1 (**7c**)		212.4 (**12c**) [37.7]	204.4 (**13c**)
R = 4-pentenyl	198.6 (**7d**)	169.7(**10d**)	212.5 (**12d**) [36.4]	204.2 (**13d**)
R = Et		166.5 (**9a**)		
R = benzyl		168.2 (**9a**)		
R = 4-pentenyl		167.4 (**9d**)		

^{a} Numbers given in parentheses are the labeling of complexes through the text. ^{b} In CDCl$_3$. ^{c} Number given in brackets are the values of J_{Rh-C} in Hz.

207−209 ppm for **1b**−**d** to 198−199 ppm for **7b**−**d**. This upfield shift for palladium(II) complexes relative to the group VI metal complexes was also observed in the related imidazol-2-ylidene species.[6d−f] The structure of **7a** was confirmed by X-ray diffraction.[11] The *trans*-biscarbene complex **7b** slowly isomerizes to the more stable *cis*-product **8**, which was synthesized by Lappert and co-workers via a different route.[13]

8 R = allyl
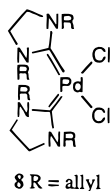
Platinum−Carbene Complexes. Unlike palladium, both carbene and carbonyl ligands were transferred from tungsten to platinum in several cases. Reactions of **1a**, **1c**, and **1d** with (PhCN)$_2$PtCl$_2$ in dichloromethane yielded **9a**, **9c**, and **9d**. The infrared carbonyl absorption appears in the range 2100−2110 cm^{-1}, which is essentially identical to that in *cis*-(R$_3$P)(CO)PtCl$_2$.[14] This

suggests a similar donating ability for diaminocarbene and trialkylphosphine ligands, which has been previously discussed.[5−8] The phosphine-substituted complex **11a,b** is obtained by treatment of **9a** or **9c** with triphenylphosphine, and the olefin-substituted complex **10d** is achieved intramolecularly via the thermal reaction of **9d** in refluxing chloroform. As with the palladium complexes, platinum biscarbenes are obtained by the treatment of the carbonyl−carbene complex **9a** with Me$_3$NO to afford **10a**. The *N*-allyl-substituted biscarbene complex **10b** is obtained directly from the reaction of **1b** with (PhCN)$_2$PtCl$_2$ in refluxing chloroform, suggesting that the formation of biscarbene metal complexes is due to the strong σ-donating property of diaminocarbenes. The chemical shift of the carbene center in **10b** (168.2 ppm) appears much upfield compared to that of the palladium complex **7b**.

^{13}C NMR data for the platinum complexes are collected in Table 2. NMR spectra of the platinum complexes **11a,b** are similar to the palladium complexes. Crystal structural determinations of **9c** and **11b** confirmed the proposed structure (see Crystallography section).

Rhodium(I)− and Gold(I)−Carbene Complexes. Carbene ligand transfer reactions were also observed with rhodium(I) and gold(I) metal ions. Substitution of a carbonyl ligand by diaminocarbene at the rhodium(I) center occurs in the reaction of **1a**, **1c**, and **1d** with

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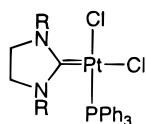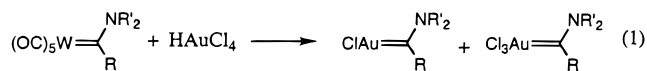
11a R = Et
11b R = benzyl

[Rh(CO)$_2$Cl]$_2$ to form biscarbene rhodium complexes **12a**, **12c**, and **12d**, respectively. With a *N*-allyl substituent, the π-coordinated product **12b** is obtained directly under the same reaction conditions. The ^{13}C NMR chemical shift of the carbene C appears around 200−215 ppm with a rhodium−carbon coupling [average $J_{Rh-C} \sim 35$ Hz].[6b,10d,15]

The gold biscarbene complexes **13a**−**d** are formed directly via the reaction of **1a**−**d** with (Me$_2$S)AuCl (Scheme 1) in dichloromethane at room temperature. The gold biscarbene complexes are similar to those prepared by the direct ligand substitution reaction of LAuCl (L = PPh$_3$, Me$_2$S) with *C*-imidazoyllithium.[16] Carbene transfer from tungsten to gold(I) has been reported by Fischer and Bock in the reaction of (CO)$_5$W= C(R)NR$'_2$ with HAuCl$_4$ (eq 1).[17] ^{13}C resonances for the carbene-carbon of **13a**−**d** (Table 2) are in the range 203−205 ppm, which is in agreement with related gold complexes.[16]

$$(OC)_5W \!=\!\! \overset{NR'_2}{\underset{R}{C}} + HAuCl_4 \longrightarrow ClAu \!=\!\! \overset{NR'_2}{\underset{R}{C}} + Cl_3Au \!=\!\! \overset{NR'_2}{\underset{R}{C}} \quad (1)$$

Carbene Transfer and Cleavage of M=C. Reaction of [Cu(CH$_3$CN)$_4$]BF$_4$ with an equimolar amount of **1a** in refluxing acetonitrile results in the cleavage of the carbene moiety to yield the imidazolidin-2-ylidinium salt **14a** quantitatively. A deuterated product at C2 is obtained when acetonitrile-d_3 or a mixture of tetrahydrofuran and D$_2$O is used. This outcome suggests that the additional hydrogen originated from the solvent. Cleavage of metal carbene is also observed in the reaction of **1a** with Cu(II) or Ag(I) ions. Therefore, the reaction of **1a** with an equimolar amount of Cu(BF$_4$)$_2$· 6H$_2$O or AgBF$_4$ in an acetonitrile solution provides **14a** as the exclusive product. Other *N*-substituted complexes such as **1b,c**, as well as group VI carbene complexes **2a,b** and **3a**−**c**, undergo similar reactions to give *N*-substituted imidazolidin-2-ylidinium salts **14a**−**c**, respectively. Treatment of **4** with an equimolar amount of [(CH$_3$CN)$_4$Cu]BF$_4$ in acetonitrle results in the cleavage of carbene ligand to yield **14b**.
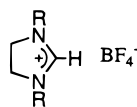
14a R = Et
14b R = allyl
14c R = benzyl

To understand the role of metal ions in these reactions, metal complexes from the reaction of **1a** with [Cu-
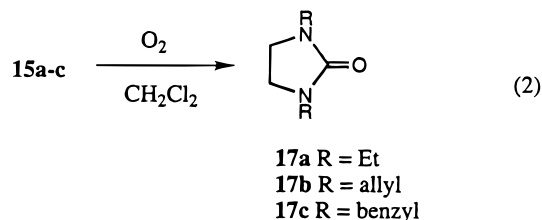
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Table 3. Some Spectroscopic Data of Copper and Silver Carbene Complexes[a]

compd	δ of M=C (carbene)	MS FAB *m/z* (cation)
15a	197.0	315{C$_{14}$H$_{28}$N$_4$^{63}Cu}
		317{C$_{14}$H$_{28}$N$_4$^{65}Cu}
15b	198.6	363{C$_{18}$H$_{28}$N$_4$^{63}Cu}
		365{C$_{18}$H$_{28}$N$_4$^{65}Cu}
15c	197.8	363{C$_{34}$H$_{36}$N$_4$^{63}Cu}
		565{C$_{34}$H$_{36}$N$_4$^{65}Cu}
16a	202.5	359{C$_{14}$H$_{28}$N$_4$^{107}Ag}
	($J_{^{107}Ag-C} = 168$ Hz,	361{C$_{14}$H$_{28}$N$_4$^{109}Ag}
	$J_{^{109}Ag-C} = 192$ Hz)	
16b	204.2	407{C$_{18}$H$_{28}$N$_4$^{107}Ag}
	($J_{^{107}Ag-C} = 169$ Hz,	409{C$_{18}$H$_{28}$N$_4$^{109}Ag}
	$J_{^{109}Ag-C} = 194$ Hz)	
16c	204.0	607{C$_{34}$H$_{36}$N$_4$^{107}Ag}
	($J_{^{107}Ag-C} = 170$ Hz,	609{C$_{34}$H$_{36}$N$_4$^{107}Ag}
	$J_{^{109}Ag-C} = 196$ Hz)	

[a] In CDCl$_3$.

(CH$_3$CN)$_4$]BF$_4$ were trapped by adding a three equimolar amount of 1,2-bis(diphenylphosphino)ethane (dppe) to the reaction mixture. A copper complex of formula of [Cu(dppe)$_2$]BF$_4$ was obtained in a quantitative yield based on the amount of copper reagent used, indicating that the copper ion retains its oxidation state. Tungsten products W(CO)$_4$(dppe), W(CO)$_3$(dppe)(CH$_3$CN), and other substitution complexes were identified by spectroscopic means. Hexacarbonyltungsten was recovered in up to 60% yield (based on the carbene complex used) when the reaction was carried out in the presence of an atmosphere of carbon monoxide.

Copper- and Silver−Carbene Complexes. A NMR tube containing a freshly dried CDCl$_3$ solution of **1a** and 0.5 mol equiv of [Cu(CH$_3$CN)$_4$]BF$_4$ was studied by both ^{1}H and ^{13}C NMR. Clean spectra were observed, consisting of peaks due to two species: the biscarbene copper species **15a** and a trace of *N,N*-diethylimidazolidinium salt **14a** (less 5% by integration). Selected ^{13}C NMR chemical shifts are summarized in Table 3. The chemical shifts and splitting patterns of copper and silver biscarbene complexes are similar to that of the stable bis(imidazol-2-ylidene) copper complex **18a**, which was isolated by Arduengo and co-workers.[5b] The range of chemical shifts for the carbene moiety in **15a**−**c** and **16a**−**c** is downfield of that in **18a,b**, reflecting a difference in π-delocalization in these *N*-heterocyclic carbenes. Unlike **18a**, the copper complexes in this work are highly sensitive toward air and moisture and readily decompose. In fact, the copper carbene complexes **15a**−**c** in dichloromethane readily convert into the corresponding cyclic urea when exposed to air (eq 2). This may be

15a-c $\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{O}_2}$ (2)

17a R = Et
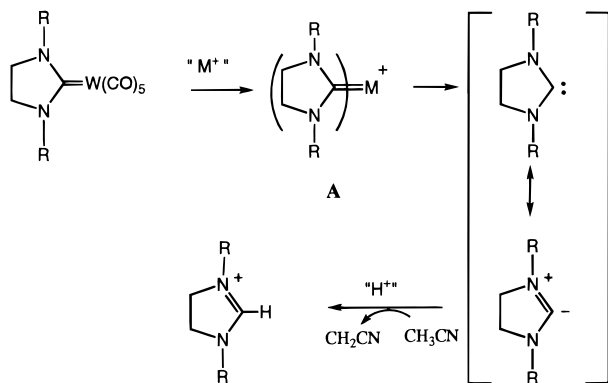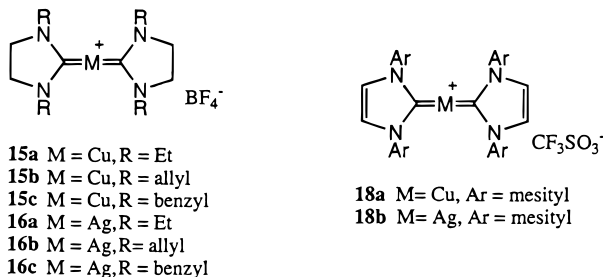17b R = allyl
17c R = benzyl

due to the less steric bulkiness of the *N*-alkyl substituents and the nonaromaticity of the *N*-heterocyclic carbene ring. Due to the contamination of trace tungsten complexes and difficulty of purification, attempts to obtain acceptable elemental analysis of these carbene complexes failed, but these copper complexes were

**Scheme 2. Proposed Reaction Pathway for M=C Cleavage**

characterized spectroscopically. The mass spectrum (FABMS) of **15a** gave cations at m/z 315, 317 in the ratio of 2:1, which accords with the ratio of natural abundance of ^{63}Cu and ^{65}Cu. Similar observations also appear with complexes **16b,c** (Table 3). The observed coupling from ^{107}Ag and ^{109}Ag nuclei to the carbene-C suggests coordination of the carbene ligands to the metal center, which is in accordance with observations by Arduengo and co-workers concerning **18b**.[5b]

15a M = Cu, R = Et
15b M = Cu, R = allyl
15c M = Cu, R = benzyl
16a M = Ag, R = Et
16b M = Ag, R = allyl
16c M = Ag, R = benzyl

18a M = Cu, Ar = mesityl
18b M = Ag, Ar = mesityl

Upon addition of a trace amount of water to the NMR samples, ^1H NMR spectra showed only the *N,N*-disubstituted imidazolidinium salt, indicating that the bis-carbene species react with water. These results are consistent with the deuterium-labeled experiments. From the above observations, the pathway of carbene cleavage shown in Scheme 2 is proposed. The first step involves a carbene-transfer reaction to form the new metal carbene complex **A**.[12] By dissociation, the diaminocarbene ligand acts as a base which receives a proton from the solvent to yield the product. It was demonstrated by theoretical calculations that the simple diaminocarbenes are strong bases, even stronger than the imidazolylidene (an aromatic heterocyclic carbene).[18,6b] Thus, when the reaction is carried out in acetonitrile, the carbene ligand deprotonates the α-proton of acetonitrile to form the organic salts **14**.

Furthermore, the cleavage reaction is accelerated under acidic conditions. In tetrahydrofuran and 10% aqueous HBF₄, reaction of **1a** with Cu(I) is complete within a few minutes. A catalytic amount of copper ions (10% mol) can accomplish the same reaction under acidic conditions. The reaction does not proceed in aqueous sodium hydroxide solution even with an excess of metal ion. When the reaction is carried out in air, the cyclic urea product and imidazolidin-2-ylidinium are

obtained (eq 3), indicating that the formation of urea stems from the reaction of copper carbene with O₂.

17a-c   **14a-c**   (3)
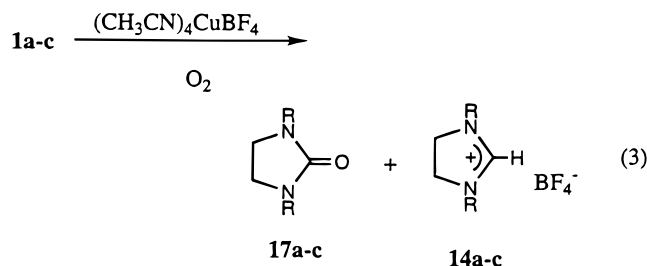
Other Carbene-Transfer Reactions. It was reported recently by Lin and co-workers[4g] that imidazol-2-ylidene silver complexes react with $(CH_3CN)_2PdCl_2$ to yield the corresponding palladium carbene. In our studies, we found that treatment of palladium complex **7b** or platinum complex **10b** with AgBF₄ readily causes the cleavage of M=C to yield **14b**. Presumably the formation of **14b** is similar to the reaction of **1**−**3** with AgBF₄, e.g., the formation of silver carbene complex **16b**, which then undergoes the cleavage reaction. No carbene ligand transfer from silver to palladium ion was observed. This result is attributed to the stronger basicity of the simple diaminocarbenes (nonaromatic heterocyclic carbene).[6b,18]

Ligand Effect. The reactivity of the diaminocarbene moiety in the transfer reaction is sensitive to the ligands around the tungsten center. It was found that **1a**, **1c**, and **4** do not react with excess S₈ in tetrahydrofuran under refluxing conditions. This is a consequence of the combination of the strongly donating character of diaminocarbene ligand and the strongly π-acid carbonyls around the tungsten center. The phosphine-substituted complexes **5a,b** and **6a,b** readily react with sulfur to form the cyclic thiourea (eq 4). Apparently, the σ-donating phosphine ligands change the electronic environment of the metal center and allow the carbene ligand to be oxidized, which is similar to the oxidative cleavage of tetraamino-substituted olefins by sulfur to form thiourea.[19,20]

19a R = Et
19b R = benzyl
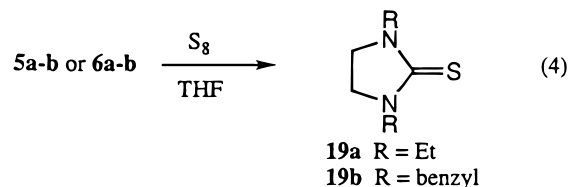
By monitoring the product formation via NMR shifts, the relative rate of the cleavage of the diaminocarbene ligand by copper(I) ion was found to decrease in the order **1a** > **4** ~ **5a** > **6a**. This may be due to the steric bulkiness of the phosphine substituent around the metal, which hinders the access of copper ion to the carbene ligand. In the carbene-transfer reaction, monodenatate phosphine-substituted carbene complexes **5a,b** undergo a similar reaction, but the phosphine ligand shifts from tungsten to the new metal center to form the phosphine−carbene complex (eq 5). Reactions of **5a,b** with $(PhCN)_2PdCl_2$ and $[(CO)_2RhCl]_2$ gave a mix-

(18) Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem.* **1991**, *95*, 4180.

(19) Maas, G.; Singer, B. *Chem. Ber.* **1983**, *116*, 3659.
(20) Schönberg, A.; Singer, E.; Stephan, W. *Chem. Ber.* **1984**, *117*, 3388.

Table 4. Crystal Data for 5b, 6b, and 11c

	5b	6b	11c
formula	$C_{39}H_{33}N_2O_4PW$	$C_{47}H_{44}Cl_2N_2O_3P_2Pt$	$C_{37}H_{37}Cl_6N_2PPt$
M_w	808.49	1001.53	948.45
wavelength (Å)	0.710 73	0.710 73	0.710 73
diffractometer	SMART CCD	SMART CCD	SMART CCD
temp (K)	295	295	295
space group	monoclinic $P2_1/n$	monoclinic $P2_1/n$	monoclinic Cc
a (Å)	9.7397(1)	9.5156(1)	19.0067(3)
b (Å)	19.1681(3)	34.0463(1)	12.6343(2)
c (Å)	18.5351(2)	14.4135(1)	16.9999(1)
α (deg)	90	90	90
β (deg)	95.986(1)	107.855(1)	101.66
γ (deg)	90	90	90
V (Å^3)	3441.48(7)	4444.68(6)	3998.07(9)
Z	4	4	4
D_{calcd} (Mg/m^3)	1.560	1.497	1.576
abs coeff (mm^{-1})	3.446	2.833	3.979
$F(000)$	1608	2008	1872
crystal size, mm^3	$0.225 \times 0.10 \times 0.07$	$0.40 \times 0.40 \times 0.20$	$0.075 \times 0.1 \times 0.2$
θ range	1.53–27.5	1.20–27.5	1.95–27.46
no. of reflns collected	63 738	57 034	12 926
no. of ind reflns	7094 ($R_{int} = 0.1104$)	10207 ($R_{int} = 0.0529$)	7685 ($R_{int} = 0.0371$)
abs corr	Sadabs	Sadabs	Semiempirical from π-scan
transmission range	0.7691–0.5743	0.6195–0.3759	0.3499–0.2309
refinement method		full-matrix least-squares on F^2	
goodness of fit on F^2	1.154	1.037	0.798
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0466$	$R_1 = 0.0621$	$R_1 = 0.0318$
	$wR_2 = 0.1035$	$wR_2 = 0.0903$	$wR_2 = 0.0573$
extinction coeff	0.000 00(6)	0.000 28(9)	0.000 03(3)
largest diff peak and hole	0.957 and 1.235 e Å^{-3}	0.840 and −1712 e Å^{-3}	0.738 and −0.522 e Å^{-3}

ture of products which were not easy to purify. However, NMR showed the disappearance of the starting carbene **5a,b**, indicating carbene transfer. In the bisphosphine-substituted carbene complexes **6a,b**, reactions gave the simple bisphosphine metal complexes **20** accompanied by formation of imidazolidin-2-ylidinium salt (eq 6).

$$ \textbf{5a-b} \xrightarrow[\text{M = Pd, Pt}]{\text{(PhCN)}_2\text{PtCl}_2} \quad (5) $$

11a R = Et
11b R = benzyl

$$ \textbf{6a-b} \xrightarrow[\text{2. NaBF}_4]{\text{1. (PhCN)}_2\text{MCl}_2} \quad (6) $$

20a M = Pd
20b M = Pt,

14a R = Et
14b R = benzyl
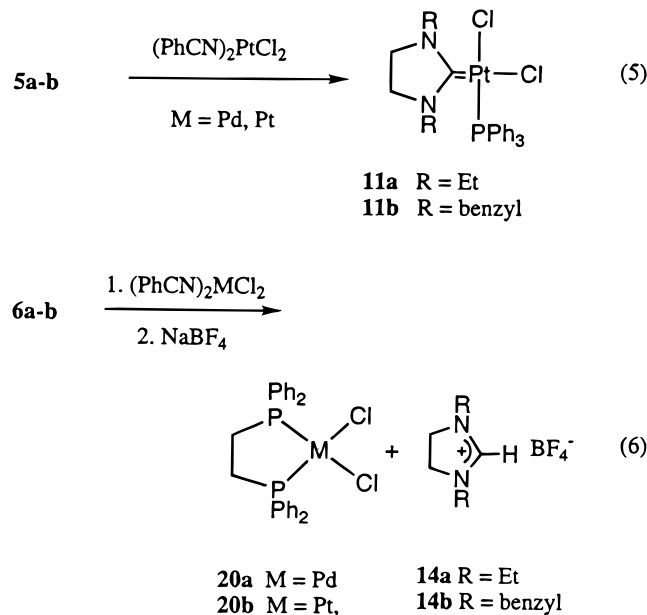
Crystallography. Single crystals suitable for X-ray analysis of complexes **1c**, **5b**, **6b·CH$_2$Cl$_2$**, **9c**, and **11b·2CH$_2$Cl$_2$** are obtained by slow evaporation of dichloromethane/hexane solutions. The crystal data are given in Tables 4 and 5. ORTEP drawings of **1c**, **5b**, **6b**, **9c**, and **11b** are depicted in Figures 1–5, respectively, and selected bond distances and bond angles are summarized in Table 6.

All tungsten complexes are octahedral. The stereochemistry of diaminocarbene and phosphine ligands is

Table 5. Crystal Data for 1c and 9c

	1c	9c
formula	$C_{22}H_{18}N_2O_5W$	$C_{18}H_{18}Cl_2N_2OPt$
space group	monoclinic $P2_1/c$	monoclinic $P2_1/c$
a (Å)	8.396(2)	20.498(4)
b (Å)	6.345(3)	10.704(3)
c (Å)	41.024(7)	8.782(2)
β (deg)	92.51(2)	101.60(2)
V (Å^3)	2183(1)	1887.6(8)
Z	4	4
D_{calcd}	1.747	1.916
$F(000)$	1108	1034
2θ range, deg	16.00–25.90	15.20–30.76
scan type	ω	$\theta/2\theta$
μ, cm^{-1}	54.359	78.032
crystal size, mm^3	$0.45 \times 0.30 \times 0.28$	$0.20 \times 0.30 \times 0.50$
scan width (deg)	$0.50 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
transmission range	0.126–0.320	0.422–1.000
no. of reflns measd	3844	3332
no. of reflns obsd^a	2903	2349
no. of unique reflns	3644	3332
computation	NRVSDP-VAX	NRVSDP-VAX
no. params	272	218
R	0.027	0.046
R_w	0.029	0.044
S	1.49	2.03

^{a} $I > 2\sigma(I)$

cis and *facial* in **5b** and **6b**, respectively. All bond distances and bond angles lie within the normal range, except that of W–C$_{carbene}$. W=C bond lengths are in the range 2.276–2.290 Å and are somewhat longer than those of Fischer-type carbenes, but are similar to those of diaminocarbene complexes,[21] indicating a resonance contribution of the amino group to the carbene center.[5-7,22] This suggests that the diaminocarbene ligand is a good σ-donor, which shortens the bond distance of carbonyl ligands *trans* to the carbene moiety (Table 6).

The platinum is square planar in complexes **9c** and **11b** (Figures 4 and 5). The bond lengths Pt=C, Pt–P,

(21) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177.
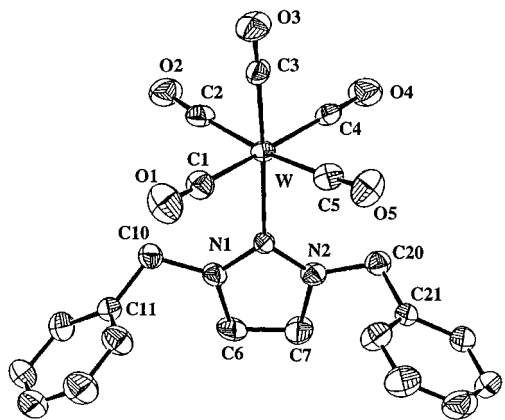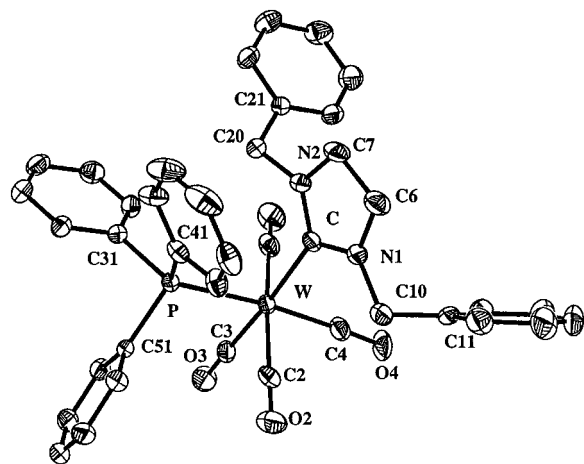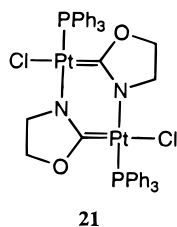
Figure 1.

Figure 2.

and Pt−Cl are typical and are in good agreement with those in platinum−aminocarbene complexes.[23] The metal to the carbene center distance in **11b** [1.970(6) Å] is slightly longer than that in **21** [1.94 Å, average].

21

Summary

Diaminocarbene transfer from a group VI metal center to another metal (Pd, Pt, Rh, Au) has been shown to be a viable synthetic approach for the preparation of metal carbene complexes. Copper and silver carbene species can be prepared similarly, but subsequently decompose to yield an iminium salt.

Experimental Section

General Information. NMR spectra were recorded on Bruker AC-E 200 or AM-300 spectrometers. Elemental analy-

Figure 3.

Figure 4.

Figure 5.

ses were determined with a Perkin-Elmer 240C instrument. Conductivities were measured in 10^{-3} M solution on a Suntex conductivity meter (SG 17A).

All reactions, manipulations, and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried with CaH_2 and distilled under nitrogen. Other chemicals and solvents were

(22) Arduengo, A. J., III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.
(23) (a) Bertani, R.; Mozzon, M.; Michelin, R. A.; Benetollo, F.; Bombieri, G.; Castilho, T. J.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **1991**, *189*, 175. (b) Manabe, N.; Yasui, M.; Nishiyama, H.; Shimamoto, S.; Matsumura, N.; Iwasaki, F. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2771.
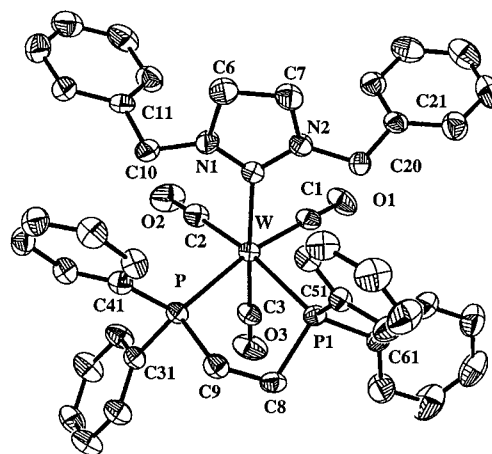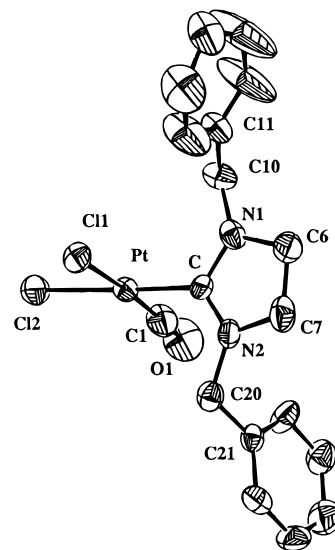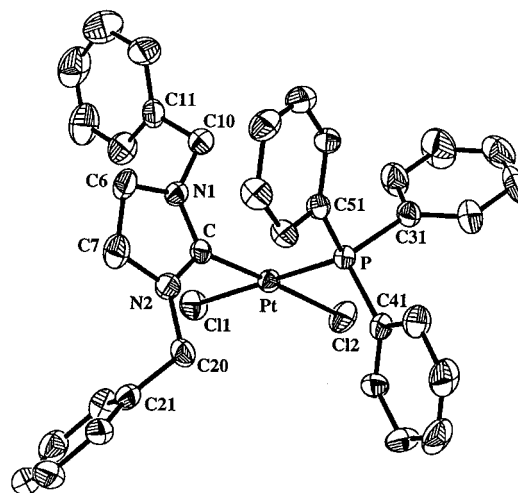
Table 6. Selected Bond Distances (Å) for 1c, 5b, 6b, 9c, and 11b

	1c, M = W	**5b**, M = W	**6b**, M = W	**9c**, M = Pt	**11b**, M = Pt
M=C	2.276(5)	2.280(6)	2.290(5)	1.97(1)	1.970(6)
M−P		2.551(2)	2.560(1)		2.242(2)
M−P1			2.512(1)		
M−C1	2.010(7)	2.015(8)	1.952(6)	1.83(2)	
M−C2	2.021(7)	2.021(8)	1.969(6)		
M−C3 (trans to carbene)	1.991(6)	1.980(7)	1.968(6)		
M−C4	2.034(6)	1.967(7)			
M−C5	2.010(7)				
C−N1	1.347(7)	1.348(8)	1.347(7)	1.37(2)	1.338(7)
C−N2	1.334(7)	1.341(7)	1.345(7)	1.33(2)	1.337(9)
M−C11				2.283(3)	2.366(2)
M−C12				2.348(4)	2.364(2)

obtained from commercial sources and used without further purification. Complexes **1a,b**, **2a,b**, **3a,b**, and **4** were prepared by a method previously reported.[11] (PhCN)$_2$PdCl$_2$ and (PhCN)$_2$PtCl$_2$ were prepared as previously described.[24]

Pentacarbonyl(1,3-dibenzylimidazolidin-2-ylidene)-tungsten (1c). A solution of (CO)$_5$W=C[NHCH$_2$]$_2$[11] (2.0 g, 5.07 mmol) and sodium hydride (1.24 g, 50.6 mmol) in THF (100 mL) was stirred at room temperature for 24 h. Benzyl chloride (2.57 g, 20.3 mmol) was added to the reaction mixture, and the resulting solution was then kept stirring for another 2 h. Water (2 mL) was slowly added to quench the excess sodium hydride at an ice-cooled temperature. After evaporation of solvent, the residue was chromatographed on silica gel (50 g). Elution with ethyl acetate/hexane (1:4) gave a yellow band, which afforded **1c** as a yellow solid (2.4 g, 83%): mp 147−149 °C (dec); IR(CH$_2$Cl$_2$) ν_{CO} =2064, 1922 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.43−7.23 (m, 10 H), 5.02 (s, 4 H, PhCH_2-), 3.32 (m, 4 H, −NCH_2-); ^{13}C NMR δ 209.1, 200.8, 197.8, 135.9, 128.8, 128.0, 127.6, 57.1, 48.1. Anal. Calcd for C$_{22}$H$_{18}$N$_2$O$_5$W: C, 46.02; H, 3.16; N, 4.88. Found: C, 45.83; H, 2.95; N, 4.89.

Pentacarbonyl[1,3-bis(4-pentenyl)imidazolidin-2-ylidene]tungsten (1d). Preparation of this compound is similar to the procedure for complex **1c** except 4-pentenyl iodide was used. Complex **1d**: yellow viscous liquid (67%); IR (CH$_2$Cl$_2$) ν_{CO} = 2062, 1919 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.78 (m, 2 H, CH$_2$CH=CH$_2$), 5.09−4.95 (m, 4 H, CH$_2$CH=CH_2), 3.69 (m, 4 H,-NCH_2−CH$_2$-), 3.54 (s, 4 H, −NCH_2-), 2.11 (m, 4 H, −CH_2−CH=CH$_2$), 1.70 (m, 4 H, −NCH$_2$CH_2CH$_2$-); ^{13}C NMR δ 207.2, 201.1, 198.0, 137.2, 115.4, 52.7, 48.0, 30.7, 27.3. Anal. Calcd for C$_{18}$H$_{22}$N$_2$O$_5$W: C, 40.77; H, 4.18; N, 5.28. Found: C, 40.47; H, 4.09; N, 5.11.

Pentacarbonyl[1,3-dibenzylimidazolidin-2-ylidene]chromium (3c). A mixture of (CO)$_5$Cr=C[NHCH$_2$]$_2$[10] (3.0 g, 11.5 mmol) and sodium hydride (1.66 g, 69.2 mmol) in THF was stirred at room temperature overnight. Benzyl chloride (3.53 g, 27.6 mmol) was added to the reaction mixture, and the resulting solution was kept stirring for another 12 h. Water (2 mL) was added slowly to quench the excess sodium hydride at an ice-cooled temperature. The organic layer was separated, and the water layer was washed with dichloromethane (20 mL × 2). The combined organic extracts were dried and concentrated. The residue was chromatographed on silica gel (100 g) with hexane/ethyl acetate (5:1) as the eluent. A light yellow band was collected and concentrated to give the desired product **3c** as a yellow solid (4.56 g, 89%): mp 172−173 °C (dec); IR(CH$_2$Cl$_2$) ν_{CO} = 2056, 1924 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.46−7.30 (m, 10 H), 5.08 (s, 4 H, PhCH_2-), 3.29 (m, 4 H, −NCH_2-); ^{13}C NMR δ 221.6, 221.5, 217.5, 136.0, 128.8, 127.9, 127.5, 55.8, 48.5. Anal. Calcd for C$_{22}$H$_{18}$N$_2$O$_5$Cr: C, 59.73; H, 4.10; N, 6.33. Found: C, 59.34; H, 3.87; N, 6.35.

General Procedure for Phosphine-Substituted Carbene Complexes. A mixture of diaminocarbene complex and an equimolar amount of phosphine was heated at 120 °C for 1 h under nitrogen. The reaction mixture was dissolved in

dichloromethane and recrystallized from dichloromethane/hexane to give the desired products as solids.

***cis*-Tetracarbonyl(1,3-diethylimidazolidin-2-ylidene)-(triphenylphosphine)tungsten (5a).** A yellow solid (96%): mp 140−141 °C (dec); IR (CH$_2$Cl$_2$) ν_{CO} = 2002, 1874, 1853 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.45−7.35 (m, 15 H, Ar−H), 3.43−3.21 (m, 8 H, −CH_2-), 1.02 (t, J = 10 Hz, 6 H); ^{13}C NMR δ 214.1 (J_{P-C} = 8.4 Hz, J_{W-C} = 93.7 Hz, W=C), 209.1, 208.4, 204.8 (W−CO), 136.9, 134.1, 130.2, 128.7, 48.1, 47.9, 13.9; ^{31}P NMR δ 25.0 (J_{P-W} = 229 Hz). Anal. Calcd for C$_{29}$H$_{29}$N$_2$O$_4$PW: C, 50.90; H, 4.27; N, 4.09. Found: C, 50.11; H, 4.17; N, 4.14.

***cis*-Tetracarbonyl(1,3-dibenzylimidazolidin-2-ylidene)-(triphenylphosphine)tungsten (5b).** A yellow solid (87%): mp 223−226 °C (dec); IR (CH$_2$Cl$_2$) ν_{CO} = 2004, 1876, 1854 (sh) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.52−7.17 (m, 25 H), 4.51 (br, 4H), 3.13 (s, 4 H); ^{13}C NMR (acetone-d_6) δ 217.6 (J_{P-C} = 6.9 Hz, W=C), 208.4, 208.1, 204.3, 137.5, 136.9, 134.2, 133.7, 130.4, 129.2, 128.9, 128.8, 128.7, 128.3, 128.1, 57.6, 48.9; ^{31}P NMR δ 24.3 (J_{P-W} = 228 Hz). Anal. Calcd for C$_{39}$H$_{33}$N$_2$O$_4$PW: C, 57.94; H, 4.11; N, 3.46. Found: C, 57.58; H, 3.99; N, 3.56.

***fac*-(1,3-Diethylimidazolidin-2-ylidene){*P,P′*-bis(diphenylphosphino)ethane}tricarbonyltungsten (6a).** A light brown solid (87%): mp 160−163 °C (dec); IR (CH$_2$Cl$_2$) ν_{CO} = 1919, 1820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.76−7.27 (m, 20 H), 3.32 (s, 4 H), 3.28 (q, J = 7.1 Hz, 4 H), 2.52 (m, 2 H), 2.18 (m, 2 H), 0.86 (t, J = 7.1 Hz, 6 H); ^{13}C NMR δ 217.8 (J_{P-C} = 8 Hz), 216.1 (J_{P-C} = 35, 10 Hz), 210.8 (J_{P-C} = 6 Hz, W=C), 137.8−128.4 (aromatic-C), 48.3, 48.2, 31.2 (J_{P-C} = 23 Hz), 13.8; ^{31}P NMR δ 36.9 (J_{P-W} = 213 Hz). Anal. Calcd for C$_{36}$H$_{38}$N$_2$O$_3$P$_2$W: C, 54.56; H, 4.83; N, 3.53. Found: C, 54.19; H, 4.72; N, 3.27.

***fac*-(1,3-Dibenzylimidazolidin-2-ylidene){*P,P′*-bis(diphenylphosphino)ethane)tricarbonyltungsten (6b).** A light brown solid (96%): mp 180−183 °C (dec); IR (CH$_2$Cl$_2$) ν_{CO} = 1921, 1824 cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.84−7.10 (m, 30 H), 4.34 (s, 4 H), 3.15 (s, 4 H), 2.63 (m, 2 H), 2.37 (m, 2 H); ^{13}C NMR δ 220.8 (J_{P-C} = 7.6 Hz), 215.6 (J_{P-C} = 34, 10 Hz), 210.2 (J_{P-C} = 6 Hz), 137.1−127.7 (aromatic-C), 52.7, 48.4, 30.4 (J_{P-C} = 18 Hz); ^{31}P NMR δ 36.1 (J_{P-W} = 213 Hz). Anal. Calcd for C$_{46}$H$_{42}$N$_2$O$_3$P$_2$W: C, 60.27; H, 4.62; N, 3.06. Found: C, 60.98; H, 4.61; N, 3.03.

General Procedure for Carbene Transfer. Diaminocarbene group VI complexes (**1−3**) and a 0.5 equimolar amount of (PhCN)$_2$PdCl$_2$, (PhCN)$_2$PtCl$_2$, [(CO)$_2$RhCl]$_2$, or (Me$_2$S)AuCl were combined in dichloromethane at room temperature for 0.5 h. During the reaction, carbon monoxide gas was released and a dark material precipitated. After filtration, ether was added to precipitate the desired carbene complex from the solution. Recrystallization of the product from dichloromethane/hexane or chromatography on silica gel with hexane/ethyl acetate as the eluent yielded the pure product. Reactions of **1a** with (PhCN)$_2$PdCl$_2$ and **1b** with (PhCN)$_2$PtCl$_2$ in equal molar ratio were carried out in refluxing chloroform. Spectral data of **7a,b**, **9a**, **10a,b**, **12a**, and **13a** as well as crystal data of **7a** and **9a** were reported previously.[12]

(24) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 61.

Bis(1,3-dibenzylimidazolidin-2-ylidene)dichloropalladium(II) (7c). A light gray solid (83%): mp 234–238 °C (dec); ^{1}H NMR (CDCl$_3$) δ 7.43 (m, 12 H), 7.25 (m, 8 H), 5.23 (s, 8 H), 3.30 (s, 8H); ^{13}C NMR δ 199.1, 136.8, 129.3, 129.2, 128.5, 53.9, 48.5. Anal. Calcd for C$_{33}$H$_{34}$N$_4$Cl$_2$Pd: C, 59.70; H, 5.16; N, 8.44. Found: C, 59.33; H, 4.89; N, 8.11.

Bis{1,3-di(4-pentenyl)imidazolidin-2-ylidene}dichloropalladium(II) (7d). A light yellow viscous liquid (96%) after chromatography on silica gel: ^{1}H NMR (CDCl$_3$) δ 5.82 (m, 4 H), 4.94 (m, 8 H), 3.98 (m, 8 H), 3.52 (s, 8 H), 2.15 (m, 8 H), 1.85 (m, 8 H); ^{13}C NMR 198.6 (Pd=*C*), 137.6, 114.9, 49.3, 48.4, 31.0, 27.3; FABMS m/z = 553.0 (M − ^{35}Cl). Anal. Calcd for C$_{26}$H$_{44}$N$_4$PdCl$_2$: C, 52.93; H, 7.52; N, 9.50. Found: C, 52.77; H, 7.50; N, 9.14.

(1,3-Dibenzylimidazolidin-2-ylidene)carbonyldichloroplatinum(II) (9c). A yellow solid (78%): mp 131–133 °C (dec); IR (CH$_2$Cl$_2$) ν_{CO} = 2106 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.35–7.21 (m, 10 H, Ar−*H*), 5.03 (m, 4 H, −C*H*$_2$Ph), 3.63 (s, 4 H); ^{13}C NMR δ 168.2 ($J_{Pt−C}$ = 1134 Hz), 154.0 ($J_{Pt−C}$ = 1735 Hz), 133.7, 129.2, 128.7, 128.2, 54.1 ($J_{Pt−C}$ = 54.0 Hz), 48.5 ($J_{Pt−C}$ = 48.7). Anal. Calcd for C$_{18}$H$_{18}$Cl$_2$N$_2$OPt: C, 39.72; H, 3.33; N, 5.15. Found: C, 39.31; H, 3.12; N, 5.25.

{1,3-Di(4-pentenyl)imidazolidin-2-ylidene}carbonyldichloroplatinum(II) (9d). A yellow solid (79%): mp 145–147 °C (dec); IR (CH$_2$Cl$_2$) ν_{CO} = 2105 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.79 (m, 2 H), 5.04 (m, 4 H), 3.87–3.63 (m, 8 H), 2.10 (m, 4 H), 1.80 (m, 4 H); ^{13}C NMR δ 167.4 (Pt=*C*), 154.4, 136.7, 115.8, 49.6, 48.6, 30.5, 26.6. Anal. Calcd for C$_{14}$H$_{22}$Cl$_2$N$_2$OPt: C, 33.61; H, 4.43; N, 5.60. Found: C, 34.11; H, 4.27; N, 5.80.

{1,3-Di(4-pentenyl)imidazolidin-2-ylidene}dichloroplatinum(II) (10d). A solution of **9d** (0.1 g, 0.2 mmol) in chloroform (5 mL) was heated to reflux for 2 h. After concentration of the reaction mixture volume to 1 mL, ether (20 mL) was added to precipitate the desired complex. Upon filtration, **9d** was obtained as a viscous yellow liquid (82 mg, 87%):^{1}H NMR (CDCl$_3$): δ 5.86–5.73 (m, 1 H), 5.04 (m, 2 H), 4.50 (m, 1 H), 3.72–3.57 (m, 1 H), 3.23–3.17 (m, 1 H), 2.30 (m, 2 H), 2.08 (m, 4 H), 1.65 (m, 2), 1.40–1.19 (2 H); ^{13}C NMR δ 169.7(Pt=*C*), 136.9, 115.6, 88.4, 69.0, 49.4, 48.7, 45.4, 31.1, 30.6, 26.7, 21.1. Anal. Calcd for C$_{13}$H$_{22}$N$_2$Cl$_2$Pt: C, 33.06; H, 4.69; N, 5.93. Found: C, 33.31; H, 4.87; N, 5.81.

***cis*-(1,3-Diethylimidazolidin-2-ylidene)(triphenylphosphine)dichloroplatinum(II) (11a).** A chloroform solution of **9a** (120 mg, 0.28 mmol) and triphenylphosphine (75 mg, 0.28 mmol) was stirred for 5 min. The reaction mixture was concentrated and the residue was recrystallized from dichloromethane/hexane to yield **11a** as a white solid (168 mg, 92%): mp 125–128 °C (dec); ^{1}H NMR (CDCl$_3$): δ 7.72–7.33 (m, 15 H), 4.18 (dq, J = 7.2, 2.4 Hz, 2 H), 3.37 (m, 2 H), 3.04 (dq, J = 7.2, 2.4 Hz, 2 H), 2.76 (m, 2 H), 1.04 (t, J = 7.2 Hz, 6 H); ^{13}C NMR δ 176.7 ($J_{P−C}$ = 6 Hz), 134.3 (d, $J_{P−C}$ = 10.6 Hz), 131.1, 128.2, 128.0, 46.7, 44.7, 12.4; ^{31}P NMR δ 9.1 ($J_{Pt−P}$ = 3970 Hz). Anal. Calcd for C$_{25}$H$_{29}$Cl$_2$N$_2$PPt: C, 45.88; H, 4.47; N, 4.28. Found: C, 45.88; H, 4.29; N, 3.95.

***cis*-(1,3-Dibenzylimidazolidin-2-ylidene)(triphenylphosphine)dichloroplatinum(II) (11b).** A solution of **9c** (272 mg, 0.5 mmol) and triphenylphosphine (131 mg, 0.5 mmol) in chloroform was stirred for 5 min. The reaction mixture was concentrated, and the residue was recrystallized from dichloromethane/hexane to yield **11b** as needlelike crystals (380 mg, 97%): mp 136–139 °C (dec); ^{1}H NMR (CDCl$_3$) δ 7.74–7.21 (m, 25 H), 5.64 (d, J = 14.1, 2 H), 3.95 (d, J = 14.1, 2 H), 3.03 (m, 2 H), 2.66 (m, 2 H); ^{13}C NMR (125 MHz) δ 178.1 ($J_{P−C}$ = 6.3 Hz), 134.5 ($J_{P−C}$ = 10 Hz), 134.4, 131.2, 129.9, 129.4, 129.0, 128.5, 128.2, 54.8, 47.1; ^{31}P NMR δ 9.69 ($J_{Pt−P}$ = 3928 Hz). Anal. Calcd for C$_{35}$H$_{33}$Cl$_2$N$_2$PPt: C, 53.99; H, 4.27; N, 3.60. Found: C, 53.97; H, 4.16; N, 3.08.

Bis(1,3-diallylimidazolidin-2-ylidene)rhodium(I) Chloride (12b). A mixture of **1b** (94.8 mg, 0.2 mmol) and [(CO)$_2$RhCl]$_2$ (19.5 mg, 0.05 mmol) in dichloromethane (20 mL) was stirred at room temperature for 48 h. The solution was filtered through Celite, and the filtrate was concentrated. The residue was dissolved in dichloromethane, and ether was added to precipitate the desired complex as a yellow solid (74%): mp 136–138 °C (dec); ^{1}H NMR (CDCl$_3$) δ 5.69–5.61 (m, 2 H), 5.28–5.10 (m, 4 H), 4.55–4.35 (m, 2 H), 3.94 (m, 4 H), 3.67–3.41 (m, 12 H), 3.12 (d, J = 11.8 Hz, 2 H), 2.85 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 202.8 ($J_{Rh−C}$ = 30.3 Hz), 131.8, 119.1, 67.3 ($J_{Rh−C}$ = 7.8 Hz), 52.9, 50.8, 50.6 ($J_{Rh−C}$ = 7.7 Hz), 49.2, 47.7; conductivity 62 Ω^{-1} cm^2 mol^{-1} (1 × 10^{-3} M in CH$_3$OH). Anal. Calcd for C$_{18}$H$_{28}$ClN$_4$Rh: C, 49.27; H, 6.43; N, 12.77. Found: C, 49.01; H, 6.02; N, 12.43.

Bis(1,3-dibenzylimidazolidin-2-ylidene)carbonylchlororhodium(I) (12c). Preparation of **12c** follows the same procedure for **12b**. A yellow solid (66%): mp 142–145 °C (dec); IR (CHCl$_3$) ν_{CO} = 1947 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.43–7.19 (m, 20 H, Ar−*H*), 5.60 (d, $^2J_{H−H}$ = 14.8 Hz, 4 H, N−CH*H*−Ph), 4.95 (d, $^2J_{H−H}$ = 14.8 Hz, 4 H, N−C*H*H−Ph), 3.99 (m, 8 H, N−C*H*$_2$-); ^{13}C NMR δ 212.4 (d, $J_{Rh−C}$ = 37.7 Hz, Rh=*C*), 187.4 (d, $J_{Rh−C}$ = 83.6), 136.8, 128.5, 128.3, 127.4, 54.6, 48.0. Anal. Calcd for C$_{35}$H$_{36}$ClN$_4$ORh: C, 63.02; H, 5.44; N, 8.40. Found: C, 62.98; H, 5.15; N, 8.22.

Bis{1,3-di(4-pentenyl)imidazolidin-2-ylidene}}carbonylchlororhodium(I) (12d). Preparation of **12c** follows the same procedure for **12b**. A yellow liquid (68%): IR (CHCl$_3$) ν_{CO} = 1942 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.82 (m, 4 H, CH$_2$=C*H*), 4.98 (m, 8 H, C*H*$_2$=C), 4.28 (m, 4 H, N−CH*H*−), 3.70 (m, 4 H, N−C*H*H−), 3.56 (m, 8 H, N−C*H*$_2$CH$_2$-), 2.11 (m, 8 H, =CHC*H*$_2$-), 1.76 (m, 8 H, NCH$_2$C*H*$_2$-); ^{13}C NMR 212.5 (d, $J_{Rh−C}$ = 36.4 Hz, Rh=*C*), 187.3 (d, $J_{Rh−C}$ = 83.0 Hz, Rh−*C*O), 138.0, 114.5, 50.0, 48.4, 31.1, 27.3; FABMS m/z [C$_{27}$H$_{44}$N$_4$O^{35}Cl^{103}Rh] = 578, 550 [M$^+$ − CO]. Anal. Calcd for C$_{27}$H$_{44}$ClN$_4$ORh: C, 56.01; H, 7.66; N, 9.68. Found: C, 56.24; H, 7.43; N, 9.33.

Bis(1,3-diallylimidazolidin-2-ylidene)gold(I) Chloride (13b). A mixture of **1b** (47.4 mg, 0.1 mmol) and (Me$_2$S)AuCl (14.7 mg, 0.05 mmol) in dichloromethane (10 mL) was stirred at room temperature for 2 h. The reaction mixture was filtered through a short column of silica gel (3 g) and washed with ethyl acetate (20 mL). The filtrate was concentrated to give **13b** as a yellow liquid (37.1 mg, 70%). ^{1}H NMR (CDCl$_3$) δ 5.79 (m, 4 H), 5.22 (m, 8 H, =C*H*$_2$), 4.15 (m, 8 H, −C*H*$_2$CH=), 3.70 (s, 8 H, −C*H*$_2$N−); ^{13}C NMR δ 205.1 (Au=*C*), 132.1, 119.1, 52.6, 49.1; FABMS m/z for [C$_{18}$H$_{28}$N$_4^{197}$Au]$^+$ = 497.1; conductivity 62 Ω^{-1} cm^2 mol^{-1} (1 × 10^{-3} M in MeOH). Anal. Calcd for C$_{18}$H$_{28}$N$_4$ClAu: C, 40.57; H, 5.30; N, 10.51. Found: C, 40.13; H, 5.56; N, 10.22.

Bis(1,3-dibenzylimidazolidin-2-ylidene)gold(I) Chloride (13c). The procedure is similar to that for **13b**. A yellow liquid (56%): ^{1}H NMR (CDCl$_3$) δ 7.24 (m 20 H), 4.73 (s, 8 H), 3.60 (s, 8 H); ^{13}C NMR δ 204.4 (Au=*C*), 134.8, 129.0, 128.4, 127.6, 54.2, 49.1; FABMS m/z for [C$_{34}$H$_{36}$N$_4^{197}$Au] = 697.1; conductivity 59 Ω^{-1} cm^2 mol^{-1} (1 × 10^{-3} M in MeOH). Anal. Calcd for C$_{33}$H$_{34}$N$_4$ClAu: C, 55.12; H, 4.77; N, 7.79. Found: C, 55.35; H, 4.66; N, 7.30.

Bis{1,3-di(4-pentenyl)imidazolidin-2-ylidene}}gold(I) Chloride (13d). The procedure is similar to that for **13b**. A yellow liquid (77%): ^{1}H NMR (CDCl$_3$) δ 5.75 (m, 4 H), 5.05 (m, 8 H), 3.69 (s, 8 H), 3.56 (t, J = 7.1 Hz, 8 H), 2.08 (m, 8 H), 1.66 (m, 8 H); ^{13}C NMR δ 204.2 (Au=*C*), 136.9, 115.7, 49.6, 48.8, 30.5, 27.2; FABMS m/z for [C$_{26}$H$_{44}$N$_4^{197}$Au]$^+$ = 609.2. Conductivity: 58 Ω^{-1} cm^2 mol^{-1} (1 × 10^{-3} M in MeOH). Anal. Calcd for C$_{26}$H$_{44}$N$_4$ClAu: C, 48.41; H, 6.87; N, 8.69. Found: C, 48.02; H, 6.55; N, 8.44.

1,3-Diethylimidazolidin-2-ylidinium Tetrafluoroborate (14a). A mixture of **1a** (300 mg, 0.67 mmol) and Cu(CH$_3$CN)BF$_4$ (210 mg, 0.67 mmol) in chloroform was heated to reflux for 4 h. After concentration of the reaction mixture, the residue was chromatographed on alumina (10 g) and eluted with dichloromethane/ethyl acetate. The desired product **14a** was obtained as a yellow liquid (121 mg, 85%): ^{1}H NMR (CDCl$_3$) δ 8.15 (s, 1 H, −NC*H*N−), 3.94 (s, 4 H), 3.55 (q, J = 7.2 Hz, 4 H), 1.31 (t, J = 7.2 Hz, 6 H); ^{13}C NMR δ 156.3, 48.1,

43.4, 12.8; ^{19}F NMR δ −153.7 (^{10}BF$_4$), −153.8 (^{11}BF$_4$). Anal. Calcd for C$_7$H$_{15}$BN$_2$F$_4$: C, 39.29; H, 7.06; N, 13.09. Found: C, 38.89; H, 6.88; N, 12.77.

1,3-Diallylimidazolidin-2-ylidinium Tetrafluoroborate (14b). This compound was obtained similarly as the procedure described for **14a**. A light yellow liquid (84%): ^{1}H NMR (CDCl$_3$) δ 8.04 (s, 1 H), 5.80 (m, 2 H), 5.30 (m, 4 H), 4.04 (d, J = 6.4 Hz), 3.88 (s, 4 H); ^{13}C NMR δ 157.3, 129.8, 121.9, 50.7, 48.1; ^{19}F NMR δ −153.0 (^{10}BF$_4$), −153.1(^{11}BF$_4$). HRFABMS Calcd for [C$_9$H$_{15}$N$_2$]$^+$ m/z = 151.1235. Found: 151.1223.

1,3-Dibenzylimidazolidin-2-ylidinium tetrafluoroborate (14c). This compound was obtained similarly as the procedure described for **14a**. A light liquid (83%); the spectral data are similar to the trifluoromethylsulonate salt reported by Maas and Singer:[16] ^{1}H NMR (CDCl$_3$) δ 8.49 (s, 1 H), 7.30−7.16 (m, 10 H), 4.68 (s, 4 H), 3.75 (s, 4 H); ^{13}C NMR δ 157.1, 132.3, 129.0, 128.7, 128.6, 51.9, 47.5; ^{19}F NMR δ −152.0 (^{10}BF$_4$), −152.1(^{11}BF$_4$). HRFABMS Calcd for [C$_{17}$H$_{19}$N$_2$]$^+$ m/z = 251.1548. Found: 251.1539.

Bis(1,3-ethylimidazolidin-2-ylidene)copper(I) Tetrafluoroborate (15a). A solution of complex **1a** (500 mg, 1.11 mmol) and [Cu(CH$_3$CN)$_4$]BF$_4$ (175 mg, 0.56 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at room temperature for 1 h. The reaction mixture was concentrated to the volume of 1 mL, and ether (30 mL) was added to cause the precipitation of white solid. After washing with ether (10 mL × 2), the white solid was collected and dried under vacuum (115 mg, 51%). This solid is extremely sensitive to moisture and slowly decomposes: mp 49−51 °C (sealed, dec); ^{1}H NMR (CDCl$_3$) δ 3.61 (s, 8 H), 3.51 (q, J = 7.6 Hz, 8 H), 1.20 (t, J = 7.6 Hz, 12 H); ^{13}C NMR δ 197.0 (Cu=C), 48.6, 45.7, 14.4; ^{19}F NMR δ −154.4 (br). HRFABMS Calcd for [C$_{14}$H$_{28}$N$_4$Cu]$^+$ m/z = 315.1612. Found: 315.1601.

Bis(1,3-allylimidazolidin-2-ylidene)copper(I) Tetrafluoroborate (15b). This complex was prepared according to the procedure described for **15a**. A white solid (58%): mp 29−32 °C; ^{1}H NMR (CDCl$_3$) δ 5.76 (m, 4 H), 5.17 (m, 8 H), 3.95 (d, J = 5 Hz, 8 H), 3.56 (s, 8 H); ^{13}C NMR δ 198.6 (Cu=C), 131.4, 117.7, 52.4, 48.6; ^{19}F NMR δ −154.0 (br). FABMS Calcd for [C$_{18}$H$_{28}$N$_4$Cu]$^+$ m/z = 363.1612. Found: 363.1601.

Bis(1,3-benzylimidazolidin-2-ylidene)copper(I) Tetrafluoroborate (15c). This complex was prepared according to the procedure described for **15a**. A white solid (69%): mp 81−82.5 °C (dec); ^{1}H NMR (CDCl$_3$) δ 7.40−7.28 (m, 20 H), 4.58 (s, 8 H), 3.59 (s, 8 H); ^{13}C NMR δ 197.8 (Cu=C), 135.2, 129.2, 128.4, 128.2, 54.6, 47.7; ^{19}F NMR δ −154.5 (br). HRFABMS Calcd for [C$_{34}$H$_{36}$N$_4$Cu]$^+$ m/z = 563.2238. Found: 563.2225.

Spectroscopic Study of Silver Carbene Complexes. A mixture of chromium carbene complex **3a,c** and an equimolar amount of AgPF$_6$ was placed in a dried NMR tube in a drybox. Purified CDCl$_3$ (0.5 mL) was added, and the sample was checked by NMR and HRFABMS.

Bis(1,3-ethylimidazolidin-2-ylidene)silver(I) Hexfluorophosphate (16a): ^{1}H NMR (CDCl$_3$) δ 3.67 (s, 8 H), 3.52 (q, J = 7.1 Hz, 8 H), 1.23 (t, J = 7.1 Hz, 12 H); ^{13}C NMR δ 202.5 (Ag=C, $J_{107Ag-C}$ = 168 Hz, $J_{109Ag-C}$ = 192 Hz), 48.4, 45.9, 14.4; ^{19}F NMR δ −74.4 (d, J_{P-F} = 713.9 Hz). HRFABMS Calcd for C$_{14}$H$_{28}$N$_4$^{107}Ag m/z = 359.1365. Found: 359.1348.

Bis(1,3-allylimidazolidin-2-ylidene)silver(I) Hexfluorophosphate (16b): ^{1}H NMR (CDCl$_3$) δ 5.86−5.77 (m, 4 H), 5.27−5.21 (m, 8 H), 4.05 (d, J = 5 Hz, 8 H), 3.65 (s, 8 H); ^{13}C NMR δ 204.2 (Ag=C, $J_{107Ag-C}$ = 169 Hz, $J_{109Ag-C}$ = 194 Hz), 132.6, 118.9, 52.1, 49.3; ^{19}F NMR δ −73.9 (d, J_{P-F} = 711.4 Hz). HRFABMS Calcd for C$_{18}$H$_{28}$N$_4$^{107}Ag m/z = 407.1365. Found: 407.1344.

Bis(1,3-benzylimidazolidin-2-ylidene)silver(I) Hexfluorophosphate (16c): ^{1}H NMR (CDCl$_3$) δ 7.31−7.18 (m, 20 H), 4.55 (s, 8 H), 3.54 (s, 8 H); ^{13}C NMR δ 203.9 (Ag=C, $J_{107Ag-C}$ = 170 Hz, $J_{109Ag-C}$ = 196 Hz), 135.3, 129.0, 128.2, 127.6, 54.8; ^{19}F NMR δ −73.5 (d, J_{P-F} = 713.3 Hz). HRFABMS Calcd for C$_{34}$H$_{36}$N$_4$^{107}Ag m/z = 607.1991. Found: 607.1987.

Reaction of Copper Carbene Complexes with O$_2$. A solution of copper carbene **16a−c** in dichloromethane was exposed to dry air with stirring for several hours. After concentration, the residue was chromatographed on silica gel with dichloromethane as eluent. The fraction containing cyclic urea was collected and concentrated to give the desired product as a light-yellow liquid. Spectral data of the cyclic urea are essentially identical to those reported in the literature: 1,3-diethylimidazolidine-2-one (**17a**),[25] 1,3-diallylimidazolidine-2-one (**17b**),[26] and 1,3-dibenzylimidazolidine-2-one (**17c**).[25]

1,3-Diethylimidazolidine-2-thione (19a). Complex **6a** (100 mg, 0.12 mmol) was treated with sulfur S$_8$ (10 mg) in dichloromethane. After stirring for 2 h, the reaction mixture was concentrated and the residue was chromatographed on silica gel (20 g) with elution by dichloromethane/ethyl acetate. The fraction containing compound **19a** was collected and concentrated to give **19a** as a white solid (15 mg, 79%): mp 61−62 °C (lit.[27] 62−63 °C); ^{1}H NMR (CDCl$_3$)[28] δ 3.65 (q, J = 7 Hz, 3.53 (s, 4 H), 1.15 (t, J = 7 Hz, 6 H); ^{13}C NMR δ 181.8, 45.3, 42.2, 12.0.

1,3-Dibenzylimidazolidine-2-thione (19b). The procedure is similar to that for **19a**. A white solid (80%): mp 85−86 °C (lit.[19] 87 °C); ^{1}H NMR (CDCl$_3$) δ 7.33−7.24 (m, 10 H), 4.88 (s, 4 H), 3.37 (s, 4 H); ^{13}C NMR 183.1, 136.5, 128.2, 127.7, 51.8, 45.3.

Reaction of Bisphosphine-Substituted Carbene Complexes with (PhCN)$_2$PdCl$_2$ and (PhCN)$_2$PtCl$_2$. A solution of **6a** or **6b** and a 0.5 equimolar amount of (PhCN)$_2$MCl (M = Pd, Pt) in dichloromethane was heated to reflux for 2 h. During the reaction period, carbon monoxide gas was released and a dark material precipitated. Excess NaBF$_4$ was added, and then the solution was filtered through silica gel (10 g) and washed with ethyl acetate. The filtrate was concentrated and dissolved in CDCl$_3$ for ^{1}H and ^{31}P NMR studies. In each case, NMR spectra show the formation of (dppe)MCl$_2$ and the iminium salt **14**. Chemical shifts of (dppe)PdCl$_2$ (**20a**)[29] and (dppe)PtCl$_2$ (**20b**)[30] are essentially identical to those reported in the literature.

Crystallography. Crystals of **1c**, **5b**, **6b**, **9c**, and **11b** were obtained by recrystallization from dichloromethane/hexane. Cell parameters of **1c** and **9c** were determined on a CAD-4 diffractometer at room temperature and by a least-squares treatment, whereas **5b**, **6b**, and **11b** were measured by a Siemens SMART CCD instrument and refined by full-matrix least-squares on F^2. The crystal data are listed in Tables 4 and 5 and selected bond distances are collected in Table 6. Other crystallographic data are supplied as Supporting Information.

Supporting Information Available: A complete description of the X-ray crystallographic structure determination of **1c**, **5b**, **6b**, **9c**, and **11b** including tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles and ^{1}H NMR spectra of **15a−c** and **16a−c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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