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Synthesis and Reactivity of Cyclometalated Rhenium Diaminocarbene Complexes

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The diaminocarbene complexes $ReBr(CO)_4\{C(NHR)(NHPh)\}$ (**1**) react with a secondary amine (Et_2NH) to yield the cyclometalated products $Re(CO)_4\{\eta^2\text{-}C(NHR)(NHC_6H_4)\}$ (**2a**, R = Pr^i; **2b**, R = Pr) via an ortho-metalation process. Treatment of the latter complexes with HBr in CH_2Cl_2 leads to the opening of the metallacyclic ring to regenerate complex **1**. The complex $Re(CO)_4\{\eta^2\text{-}C(NHPr^i)(NHC_6H_4)\}$ (**2a**) reacts with iodine to afford $ReI(CO)_4\{C(NHPr^i)(NHC_6H_4I)\}$ (**3**), which on reaction with secondary amine induces the successive intramolecular activation of a C–H bond to form $Re(CO)_4\{\eta^2\text{-}C(NHPr^i)(NHC_6H_3I)\}$ (**4**). Treatment of **4** with iodine leads to the reopening of the Re–C σ bond to yield the iodo complex $ReI(CO)_4\{C(NHPr^i)(NHC_6H_3I_2)\}$ (**5**). Complex **2a** reacts with the Brønsted acid CH_3CO_2H or CF_3CO_2H in CH_2Cl_2 to give the addition products $Re(CO)_4(\eta^1\text{-}OCOR)\{C(NHPr^i)(NHPh)\}$ (**6a**, R = CH_3; **6b**, R = CF_3). Treatment of **2a** with $HC\equiv CCO_2H$ in CH_2Cl_2 leads to the formation of both the complex $Re(CO)_4(\eta^1\text{-}OCOC\equiv CH)\{C(NHPr^i)(NHPh)\}$ (**6c**) and the minor species $ReCl(CO)_4\{C(NHPr^i)(NHPh)\}$ (**7**). Molecular structures of **3**, **6c**, and **7** have been determined by X-ray diffraction studies. Crystal data are as follows: **3**, *Pbcn*, a = 7.419(3) Å, b = 16.52(6) Å, c = 32.215(21) Å, V = 3948(14) Å^3, Z = 8, R = 8.2%, R_w = 10.2%; **6c**, $P2_1/n$, a = 9.9905(13) Å, b = 12.7994(14) Å, c = 15.0592(16) Å, β = 96.035(10)°, V = 1915.0(4) Å^3, Z = 4, R = 4.1%, R_w = 5.0%; **7**, $P2_1/c$, a = 15.6532(23) Å, b = 6.4584(14) Å, c = 17.4384(20) Å, β = 107.924(11)°, V = 1677.4(5) Å^3, Z = 4, R = 4.4%, R_w = 5.0%.

Introduction

In recent years there has been a major effort to explore intramolecular metalation reactions in view of their relevance to catalysis[1] and organic synthesis.[2] Though many metallacyclic compounds with five-membered rings have been reported, most of them occurred on metal complexes containing cyclometalated ligands with phosphorus, nitrogen, sulfur, and oxygen as the donor atoms.[3] However, there are isolated reports concerning such reactions in metal carbene complexes containing cyclometalated ligands with carbon as the donor atom.[4] With the objective of evaluating the influence of isocyanide–carbonyl replacement on the reactivity of metal complexes,[5] we have previously reported a synthetic strategy for the preparation of isocyanide complexes by the ylide-type reaction of metal carbonyls with phosphine imides[6] and the synthesis of diaminocarbene (amidinium) complexes $ReBr(CO)_4\{C(NHR)(NHPh)\}$ (**1**).[7] As communicated earlier,[8] we describe in detail herein the unusual intramolecular activation of a C–H bond in these diaminocarbene complexes, in which ortho metalation of the diaminocarbene ligand occurs easily, and the subsequent Re–C σ bond of the cyclometalated ring is reactive and is cleaved readily. We also extend the study of reactions of the cyclometalated complexes to include protic acids. Utilizing the reactive Re–C σ bond, the cyclometalated complex provides a convenient starting material for the formation of rhenium complexes with a diaminocarbene moiety.

Results and Discussion

Preparation of the Cyclometalated Carbene Complex $Re(CO)_4\{\eta^2\text{-}C(NHR)(NHC_6H_4)\}$. Reaction of the diaminocarbene (amidinium) complexes $ReBr(CO)_4\{C(NHR)(NHPh)\}$ (**1a**, R = Pr^i; **1b**, R = Pr) with Et_2NH in CH_2Cl_2 gives moderate yields of the cyclometalated complexes $Re(CO)_4\{\eta^2\text{-}C(NHR)(NHC_6H_4)\}$ (**2a**, R = Pr^i; **2b**, R = Pr) via an ortho-metalation process (eq 1). The ^1H NMR spectrum of **2a** showed three well-separated multiplets centered at δ 7.69 (1 H), 6.96 (1 H), and 6.80 (2 H) corresponding to four protons of the metalated C_6H_4 group.[3d] This region of resonances is diagnostic of metalation of the phenyl group at the ortho position. The

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(1) (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (b) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743. (c) Santra, P. K.; Saha, C. H. *J. Mol. Catal.* **1987**, *39*, 279. (d) Bose, A.; Saha, C. H. *J. Mol. Catal.* **1989**, *49*, 271.

(2) Ryabov, A. D. *Synthesis* **1985**, 233.

(3) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 298–300. (b) Bruce, M. I. *Angew, Chem., Int. Ed. Engl.* **1977**, *16*, 73. (c) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1972**, *40*, 393. (d) Colbran, S. B.; Irele, P. T.; Johnson, B. F. G.; Lahoz, F. J.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2023. (e) Lahuerta, P.; Payá, J.; Solans, X.; Ubeda, M. A. *Inorg. Chem.* **1992**, *31*, 385. (f) Joslin, F. L.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 521. (g) McKinney, R. J.; Firestein, G.; Kaesz, H. D. *Inorg. Chem.* **1975**, *14*, 2057. (h) Alper, H. *J. Organomet. Chem.* **1973**, *61*, C62. (i) Lugan, N.; Bonnet, J. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4484.

(4) Muir, K. W.; Walker, R.; Chatt, J.; Richards, R. L.; Royston, G. H. D. *J. Organomet. Chem.* **1973**, *56*, C30.

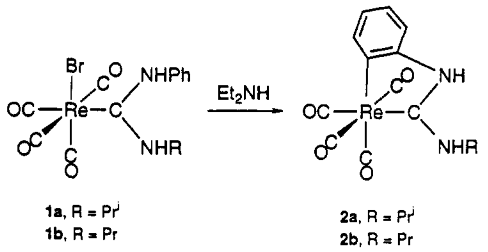
(5) (a) Lin, Y. W.; Gau, H. M.; Wen, Y. S.; Lu, K. L. *Organometallics* **1992**, *11*, 1445. (b) Lu, K. L.; Chen, C. J.; Lin, Y. W.; Gau, H. M.; Hong, F. E.; Wen, Y. S. *Organometallics* **1993**, *12*, 2188. (c) Lu, K. L.; Su, C. J.; Lin, Y. W.; Gau, H. M.; Wen, Y. S. *Organometallics* **1992**, *11*, 3832.

(6) (a) Abel, E. W.; Mucklejohn, S. A. *Phosphorus Sulfur Relat. Elem.* **1981**, *9*, 235 and references therein. (b) Kiji, J.; Matsumura, A.; Haishi, T.; Okazaki, S.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2731. (c) Alper, H.; Partis, R. A. *J. Organomet. Chem.* **1972**, *35*, C40. (d) Mirkin, C. A.; Lu, K. L.; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 7279. (e) Mirkin, C. A.; Lu, K. L.; Snead, T. E.; Young, B. A.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 3800.

(7) Chen, L. C.; Chen, M. Y.; Chen, J. H.; Wen, Y. S.; Lu, K. L. *J. Organomet. Chem.* **1992**, *425*, 99.

(8) Lu, K. L.; Wang, C. M.; Lee, H. H.; Chen, L. C.; Wen, Y. S. *J. Chem. Soc., Chem. Commun.* **1993**, 706.

0276-7333/94/2313-0593$04.50/0

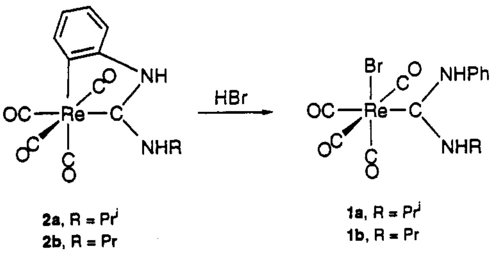


(1)

^{13}C NMR spectrum showed a downfield resonance peak at δ 154.53 which provided evidence for the presence of a metal–carbon σ bond in this type of complex.[9] In addition to spectroscopic determination, the structure of **2b** was characterized by single-crystal X-ray diffraction analysis and described in a previous communication.[8]

The formation of a metal–carbon σ bond usually occurs by direct interaction of the metal substrate and ligand and elimination of the hydrogen by combination with a suitable leaving group. It has been noted that the presence of bulky groups promotes the metalation process, as observed in many complexes containing tertiary phosphanes.[3b,10] A view of the crystal structure of $ReBr(CO)_4\{C(NHPr^i)(NHPh)\}$ (**1a**) leads to the suggestion that the steric bulk of the diaminocarbene group may play an important role in placing the phenyl proton closer to the bromine atom.[7] This is corroborated by the observation that the ortho-metalation reaction of $ReBr(CO)_4\{C(NHPr^i)(NHPh)\}$ (**1a**) with a more bulky isopropyl group proceeds more readily than that of $ReBr(CO)_4\{C(NHPr)(NHPh)\}$ (**1b**) with the propyl ligand, illustrating that the steric hindrance of the diaminocarbene ligand may be responsible for the transformation observed.

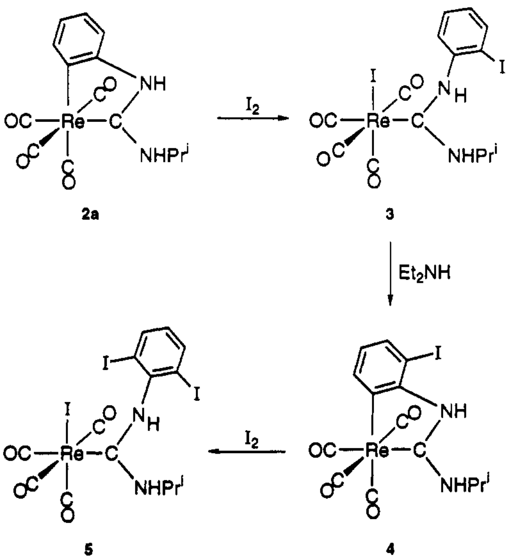
Cleavage of the Cyclometalated Re–C σ Bond of 2. The unexpected formation of the diaminocarbene complexes containing a cyclometalated ligand with carbon as the donor atom prompted us to extend the studies of their chemical behavior. Bubbling HBr gas through a solution of complex **2** in CH_2Cl_2 gives complex **1** in near-quantitative yield at room temperature (eq 2). Treatment of complex 2 in CH_2Cl_2 with aqueous HBr affords the same results. The reactive cyclometalated Re–C σ bond of **2** is demonstrated by its facile reversible insertion reaction with HBr.



(2)

As illustrated in Scheme 1, complex **2a** has been found to react with I_2 in CH_2Cl_2 at room temperature to yield the complex $ReI(CO)_4\{C(NHPr^i)(NHC_6H_4I)\}$ (**3**) in moderate yield. It was isolated as a microcrystalline solid and has been spectroscopically characterized. As anticipated, the carbonyl stretching frequencies observed in the IR spectrum of **3** (2100 (m), 2000 (vs), and 1932 (s) cm^{-1}) are similar to those of the diaminocarbene complex **1** (2104 (m), 2001 (vs), and 1931 (s) cm^{-1}).[7] Complex **3** exists as two isomeric forms in equilibrium in solution at room temperature, as evidenced by the ^1H NMR spectrum. The isomerization is likely to occur by rotation about the C–N bond[5,11,12] in the diaminocarbene ligand in solution. The homonuclear COSY 2D spectrum shows three well-separated multiplets centered at δ 7.96, 7.90 (1 H, two isomers), 7.43 (1 H), and 7.18 (2 H) corresponding to four protons of the C_6H_4I group. In addition to spectroscopic characterization, an X-ray crystal analysis of complex **3** has been undertaken (Figure 1). Pertinent crystallographic details are set out in Tables 2 and 3. The complex **3** crystallizes in the space group *Pbcn*. Pseudooctahedral geometry is observed around the Re atom. C(5) of the carbene ligand appears as an sp^2 hybrid with a distorted-trigonal-planar arrangement. The bond angle of Re–C(5)–N(1) (128.3(14)°) appears larger than that of Re–C(5)–N(2) (117.5(16)°) and N(1)–C(5)–N(2) (114.2(19)°) due to the steric requirement for the arrangement of the diaminocarbene group. The iodine and the diaminocarbene groups are *cis* to each other. C(5)–N(1) and C(5)–N(2) show partial double-bond character (1.32(3) and 1.36(3) Å, respectively).

Scheme 1



The cyclometalation process can be reversed by incorporating HBr or I_2 into the rhenium–carbon σ bond. The formation of complex **3** is interesting, since the reopening of the Re–C σ bond of the cyclometalated ring takes place under very mild conditions. These reactions are believed to proceed via the electrophilic attack of iodine[13] at the cyclometalated Re–C σ bond similar to the reaction with HBr. The severe distortion of the cyclometalated ring may be responsible for the cleavage of the Re–C σ bond.

Successive Closing and Opening of the Cyclometalated Ring. Interestingly, the diaminocarbene complex $ReI(CO)_4\{C(NHPr^i)(NHC_6H_4I)\}$ (**3**) undergoes further intramolecular C–H activation to form a cyclometalated complex. Complex **3** readily reacts with Et_2NH in CH_2Cl_2 at room temperature to yield the ortho-metalated complex $Re(CO)_4\{\eta^2\text{-}C(NHPr^i)(NHC_6H_3I)\}$ (**4**) in 48% yield (Scheme 1). The IR spectrum shifts slightly (about 3 cm^{-1}) to higher frequency but retains the same pattern

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[9] Garber, A. R.; Garrou, P. E.; Hartwell, G. E.; Smas, M. J.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1975**, *86*, 219.

[10] Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856.

[11] Lukehart, C. M. In *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985; pp 197–201.

[12] Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123.

[13] Ingham, W. L.; Coville, N. J. *Organometallics* **1992**, *11*, 2551.

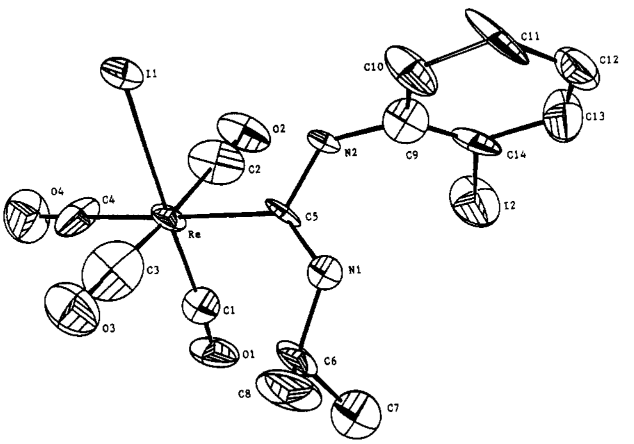


Figure 1. ORTEP diagram of ReI(CO)$_4${C(NHPr^i)(NHC$_6$H$_4$I)} (3).

Table 1. Crystal and Intensity Collection Data for ReI(CO)$_4${C(NHPr^i)(NHC$_6$H$_4$I)} (3), Re(CO)$_4$(η^1-OCOC≡CH){C(NHPr^i)(NHPh)} (6c), and ReCl(CO)$_4${C(NHPr^i)(NHPh)} (7)

formula	$C_{14}H_{13}I_2N_2O_4Re$	$C_{17}H_{15}N_2O_6Re$	$C_{14}H_{14}ClN_2O_4Re$
fw	713.28	529.52	495.94
space group	*Pbcn*	$P2_1/n$	$P2_1/c$
a, Å	7.419(3)	9.9905(13)	15.6532(23)
b, Å	16.52(6)	12.7994(14)	6.4584(14)
c, Å	32.215(21)	15.0592(16)	17.4384(20)
β, deg		96.035(10)	107.924(11)
V, Å^3	3948(14)	1915.0(4)	1677.4(5)
D_{calc}, g cm^{-3}	2.400	1.837	1.964
Z	8	4	4
μ(Mo Kα), cm^{-1}		64.6	75.2
μ(Cu Kα), cm^{-1}	366.3		
temp	room temp	room temp	room temp
radiation	Cu Kα	Mo Kα	Mo Kα
2θ (max)	118.9	44.9	49.8
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
total no. of reflns	2828	2670	3063
no. of obsd reflns	1986 ($F_o > 2.5\sigma(F_o)$)	2073 ($F_o > 2\sigma(F_o)$)	2021 ($F_o > 2\sigma(F_o)$)
no. of obsd variables	209	236	199
R	0.082	0.041	0.044
R_w	0.102	0.050	0.050
$\Delta(\rho)$, e Å^{-3}	3.980	2.770	2.280
Δ/σ_{max}	0.017	0.001	0.001
GOF	3.47	2.53	2.12

integrity as that of the ortho-metalated complex 2. The ^{1}H NMR spectrum showed three sets of peaks centered at δ 7.62, 7.32, and 6.52 in the phenyl region, which is diagnostic of metalation of the C_6H_3I group at the ortho position.

It is worth noting that the Re–C σ bond of the cyclometalated ring of complex 4 is also reactive. The opening of the Re–C σ bond has been achieved by reacting the latter with iodine in CH_2Cl_2 at room temperature to yield ReI(CO)$_4${C(NHPr^i)(NHC$_6$H$_3$I$_2$)} (5). The FAB MS spectrum of 5 exhibited the molecular ion at *m/z* 840 as well as the CO-loss and iodine-loss fragments. The IR spectrum showed that the absorption pattern and the resonance frequency in the ν_{CO} stretching region are very similar to those of ReI(CO)$_4${C(NHPr^i)(NHC$_6$H$_4$I)} (3), indicating that the transformation of the phenyl group containing one more iodine atom does not alter the ν_{CO} stretching environment of the metal center. The ^{1}H NMR spectrum showed that the phenyl moiety is a 2,6-diiodo-1-aminophenyl group with the characteristic resonances for the three protons in the aromatic phenyl region. The hindered rotation about the C–N bond in the diaminocarbene ligand may be responsible for the existence of two isomeric forms in 20:1 ratio in solution for complex 5.[5,11,12] Particularly interesting is the formtion of a diaminocarbene moiety containing a 2,6-diiodo-1-aminophenyl group in complex 5 via ortho metalation and the reverse process, since the preparation of a 2,6-diiodo-1-aminophenyl group is difficult by general organic methods.

Table 2. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for ReI(CO)$_4${C(NHPr^i)(NHC$_6$H$_4$I)} (3)

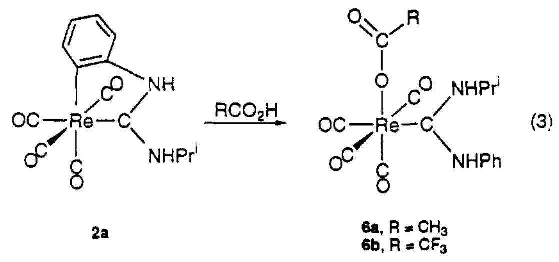
atom	*x*	*y*	*z*	B_{iso}[a]
Re	0.02716(15)	0.12267(7)	0.33979(3)	2.65(5)
I(1)	−0.12986(23)	0.22411(10)	0.40085(5)	3.56(8)
I(2)	0.22209(31)	−0.14332(14)	0.42318(7)	6.18(11)
N(1)	−0.1546(24)	−0.0448(11)	0.3639(5)	2.3(8)
N(2)	−0.0354(24)	0.0216(11)	0.4183(5)	2.3(8)
O(1)	0.1972(23)	0.0128(12)	0.2752(6)	4.7(9)
O(2)	0.3836(27)	0.1131(14)	0.3893(6)	5.8(12)
O(3)	−0.3468(29)	0.1398(13)	0.2953(7)	6.1(12)
O(4)	0.1766(30)	0.2695(13)	0.2912(7)	6.7(12)
C(1)	0.1283(37)	0.0496(16)	0.2995(7)	3.4(12)
C(2)	0.2570(36)	0.1177(20)	0.3704(10)	5.4(17)
C(3)	−0.2084(39)	0.1324(20)	0.3133(12)	6.1(19)
C(4)	0.1203(43)	0.2144(16)	0.3093(9)	5.2(16)
C(5)	−0.0695(27)	0.0204(15)	0.3767(6)	2.2(10)
C(6)	−0.2104(35)	−0.0637(16)	0.3216(7)	3.4(12)
C(7)	−0.1240(51)	−0.1423(18)	0.3062(7)	5.9(18)
C(8)	−0.4122(40)	−0.0700(21)	0.3190(10)	5.8(16)
C(9)	−0.0987(30)	−0.0369(15)	0.4486(6)	2.6(11)
C(10)	−0.2358(32)	−0.0175(18)	0.4723(7)	4.3(13)
C(11)	−0.2962(40)	−0.0664(23)	0.5042(7)	5.6(17)
C(12)	−0.2235(41)	−0.1421(18)	0.5092(8)	4.1(14)
C(13)	−0.0750(45)	−0.1605(17)	0.4869(10)	5.1(16)
C(14)	−0.0136(35)	−0.1062(18)	0.4551(7)	3.6(13)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 3. Selected Bond Distances and Angles for ReI(CO)$_4${C(NHPr^i)(NCH$_5$H$_4$I))} (3)

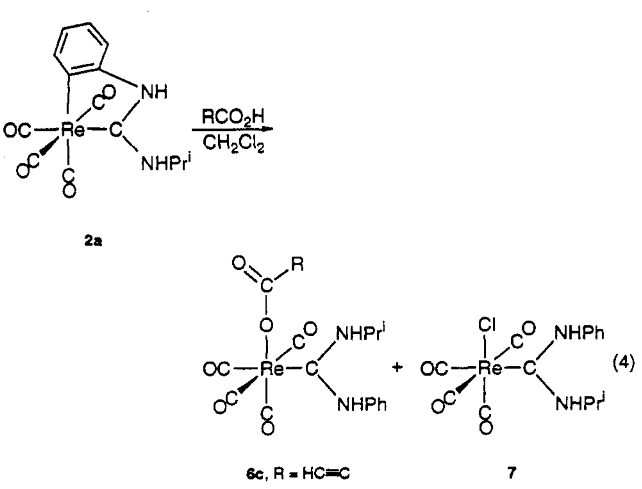
(a) Bond Distances (Å)			
Re–I(1)	2.834(4)	Re–C(1)	1.925(24)
Re–C(2)	1.97(3)	Re–C(3)	1.95(3)
Re–C(4)	1.93(3)	Re–C(5)	2.187(23)
I(2)–C(14)	2.120(25)	N(1)–C(5)	1.32(3)
N(1)–C(6)	1.46(3)	N(2)–C(5)	1.36(3)
N(2)–C(9)	1.45(3)	O(1)–C(1)	1.12(3)
O(2)–C(2)	1.12(4)	O(3)–C(3)	1.19(4)
O(4)–C(4)	1.16(4)		
(b) Bond Angles (deg)			
I(1)–Re–C(1)	177.4(8)	I(1)–Re–C(2)	91.9(9)
I(1)–Re–C(3)	83.5(10)	I(1)–Re–C(4)	92.1(8)
I(1)–Re–C(5)	86.8(6)	C(1)–Re–C(2)	88.5(12)
C(1)–Re–C(3)	96.1(12)	C(1)–Re–C(4)	90.5(11)
C(1)–Re–C(5)	90.6(10)	C(2)–Re–C(3)	175.4(13)
C(2)–Re–C(4)	88.7(14)	C(2)–Re–C(5)	88.9(11)
C(3)–Re–C(4)	91.9(14)	C(3)–Re–C(5)	90.4(11)
C(4)–Re–C(5)	177.3(11)	N(2)–C(9)–C(10)	118.7(23)
C(5)–N(1)–C(6)	127.2(18)	N(2)–C(9)–C(14)	121.9(20)
C(5)–N(2)–C(9)	126.2(18)	Re–C(1)–O(1)	173.7(23)
Re–C(2)–O(2)	176(3)	Re–C(3)–O(3)	176(3)
Re–C(4)–O(4)	179(3)	Re–C(5)–N(1)	128.3(14)
Re–C(5)–N(2)	117.5(16)	N(1)–C(5)–N(2)	114.2(19)
I(2)–C(14)–C(9)	124.4(19)	I(2)–C(14)–C(13)	115.3(21)

Reaction of Complex 2a with Brønsted Acids. Treatment of complex 2a with Brøsted acids RH at room temperature yields Re(CO)$_4$(η^1-OCOR){C(NHPr^i)(NHPh)} (6a, R = CH_3; 6b, R = CF_3; 6c, R = C≡CH) (eqs 3 and 4) in moderate yields. They were isolated as microcrystalline solids and have been spectroscopically characterized. The IR spectrum of 6c showed terminal ν_{CO} stretching frequencies at 2105 (m), 1998 (vs), and 1928 (s) cm^{-1}, similar to those of the diaminocarbene complexes 1



and 3. The mass spectrum showed the molecular ion at *m/z* 530 followed by peaks corresponding to the successive loss of carboxylate fragment and four carbonyls, consistent with the indicated formulation. The ^{1}H NMR spectrum showed that complex **6** also exists as two isomeric forms in solution at room temperature. Single crystals of Re(CO)$_4$(η^1-OCOC≡CH){C(NHPr^i)(NHPh)} (**6c**) were grown from hexane/CH$_2$Cl$_2$ solvent, and an X-ray diffraction analysis was performed. The crystal structure is fully consistent with the spectroscopic data for **6c**. An ORTEP representation is shown in Figure 2, and pertinent crystallographic details are set out in Tables 4 and 5. Pseudooctahedral geometry is observed around the Re atom. The carboxylate group HC≡CCO$_2$ binds to the Re center with a unidentate-O coordination mode and contains a C≡C triple bond (C(6)–C(7) = 1.160(21) Å). The carboxylate and the diaminocarbene groups are *cis* to each other. The orientations of the phenyl group of the diaminocarbene ligand and the carboxylate ligand are in opposite directions, which is likely to be attributed to the steric repulsion between these two groups. C(8)–N(1) and C(8)–N(2) show partial double-bond character with bond lengths of 1.327(15) and 1.337(13) Å, respectively. The dihedral angle of O(5)–Re–C(8)–N(1) is 14.9(5)°. The three CO ligands *cis* to the carboxylate group have slightly longer Re–C(CO) distances (2.016(18), 2.003(15), and 1.987(14) Å) than the *trans* CO ligand (1.926(15) Å). This may be due to the different degree of back-bonding of electron density on Re to the CO ligands, in accord with the slight or nonexistent π-electron-accepting ability of the carboxylate group.[14,15]

Complex **2a** reacts with propynoic acid in CH$_2$Cl$_2$ at room temperature to yield not only the major species **6c** but also the minor complex ReCl(CO)$_4${C(NHPr^i)(NHPh)} (**7**) (eq 4). The IR spectrum of **7** showed the same absorption pattern and similar resonance frequencies in the ν_{CO} stretching region as those of the related complexes **1**, **3**, and **5**. Complex **7** also exists as two isomeric forms in equilibrium in solution in a 10:1 ratio. This observation is also similar to that for complexes **1**, **3**, and **5**. The mass spectrum of **7** showed the molecular ion at *m/z* 496 as well



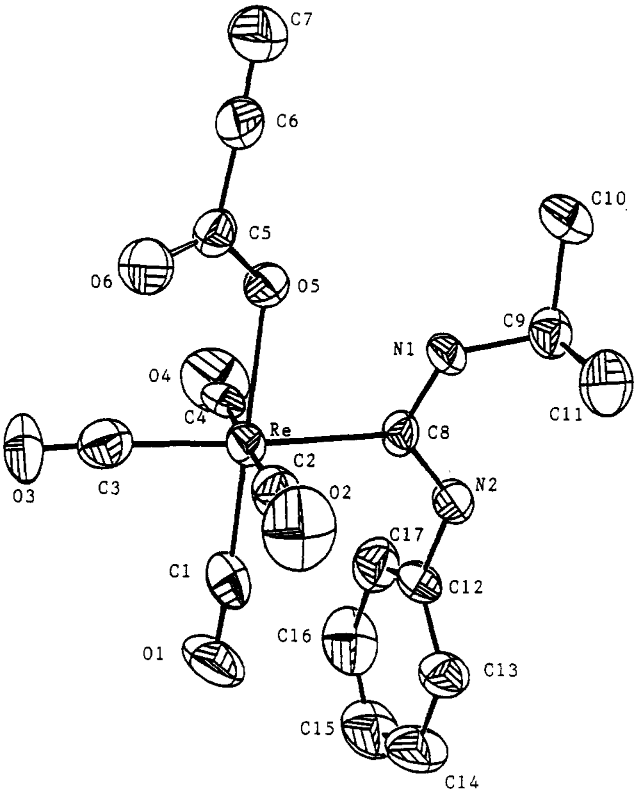


Figure 2. ORTEP diagram of Re(CO)$_4$(η^1-OCOC≡CH){C(NHPr^i)(NHPh)} (**6c**).

Table 4. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for Re(CO)$_4$(η^1-OCOC≡CH){C(NHPr^i)(NHPh)} (6c)

atom	*x*	*y*	*z*	B_{iso}[a]
Re	0.07913(5)	0.20383(4)	0.14547(3)	2.907(22)
N(1)	−0.0025(9)	0.3206(7)	0.3082(5)	3.1(4)
N(2)	0.2064(9)	0.2548(7)	0.3447(6)	3.1(4)
O(1)	0.3160(10)	0.0504(8)	0.1589(7)	6.2(5)
O(2)	−0.0823(12)	0.0241(9)	0.2265(7)	7.0(6)
O(3)	0.0199(11)	0.1090(8)	−0.0447(5)	6.2(6)
O(4)	0.2591(12)	0.3857(8)	0.0798(7)	6.7(6)
O(5)	−0.0929(8)	0.3091(6)	0.1326(5)	3.7(4)
O(6)	−0.2323(9)	0.2147(7)	0.0381(5)	4.3(4)
C(1)	0.2316(14)	0.1110(11)	0.1562(8)	4.1(6)
C(2)	−0.0282(13)	0.0894(11)	0.1947(8)	4.1(6)
C(3)	0.0374(13)	0.1457(11)	0.0234(9)	4.2(6)
C(4)	0.1901(15)	0.3205(12)	0.1010(8)	4.6(7)
C(5)	−0.2016(12)	0.2937(10)	0.0832(7)	3.2(6)
C(6)	−0.2947(13)	0.3802(11)	0.0820(8)	4.0(6)
C(7)	−0.3675(16)	0.4510(13)	0.0798(10)	6.1(8)
C(8)	0.1023(12)	0.2693(8)	0.2825(7)	2.7(5)
C(9)	−0.0187(11)	0.3626(10)	0.3966(7)	3.4(6)
C(10)	−0.1175(13)	0.4533(11)	0.3864(8)	4.7(6)
C(11)	−0.0676(14)	0.2782(11)	0.4556(8)	5.0(7)
C(12)	0.3349(11)	0.2122(9)	0.3307(7)	3.1(5)
C(13)	0.3775(13)	0.1227(10)	0.3745(8)	4.1(6)
C(14)	0.5054(16)	0.0836(13)	0.3653(11)	6.1(8)
C(15)	0.5894(15)	0.1358(15)	0.3146(11)	6.3(9)
C(16)	0.5484(15)	0.2269(15)	0.2728(10)	5.9(9)
C(17)	0.4178(14)	0.2675(11)	0.2823(8)	4.7(7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

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(14) (a) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398. (b) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudaroski, R. *Inorg. Chem.* **1982**, *21*, 1656. (c) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704.

(15) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

Table 5. Selected Bond Distances and Angles for $\mathrm{Re(CO)_4(\eta^1\text{-}OCOC{\equiv}CH)\{C(NHPr^i)(NHPh)\}}$ (6c)

(a) Bond Distances (Å)			
Re–O(5)	2.176(7)	Re–C(1)	1.926(15)
Re–C(2)	2.003(15)	Re–C(3)	1.987(14)
Re–C(4)	2.016(18)	Re–C(8)	2.217(10)
N(1)–C(8)	1.327(15)	N(1)–C(9)	1.461(14)
N(2)–C(8)	1.337(13)	N(2)–C(12)	1.430(15)
O(1)–C(1)	1.143(18)	O(2)–C(2)	1.129(19)
O(3)–C(3)	1.124(16)	O(4)–C(4)	1.149(21)
O(5)–C(5)	1.266(14)	O(6)–C(5)	1.238(15)
C(5)–C(6)	1.445(19)	C(6)–C(7)	1.160(21)
(b) Bond Angles (deg)			
O(5)–Re–C(1)	179.7(4)	O(5)–Re–C(2)	92.2(4)
O(5)–Re–C(3)	93.6(4)	O(5)–Re–C(4)	88.2(4)
O(5)–Re–C(8)	81.6(3)	C(1)–Re–C(2)	88.1(5)
C(1)–Re–C(3)	86.2(5)	C(1)–Re–C(4)	91.6(5)
C(1)–Re–C(8)	98.7(4)	C(2)–Re–C(3)	90.0(5)
C(2)–Re–C(4)	177.7(5)	C(2)–Re–C(8)	86.5(4)
C(3)–Re–C(4)	92.3(5)	C(3)–Re–C(8)	173.9(5)
C(4)–Re–C(8)	91.2(4)	C(8)–N(1)–C(9)	127.9(9)
C(8)–N(2)–C(12)	126.4(9)	Re–O(5)–C(5)	125.2(7)
Re–C(1)–O(1)	174.7(10)	Re–C(2)–O(2)	175.8(11)
Re–C(3)–O(3)	176.0(11)	Re–C(4)–O(4)	175.9(11)
O(5)–C(5)–O(6)	126.7(11)	O(5)–C(5)–C(6)	113.5(11)
O(6)–C(5)–C(6)	119.8(10)	C(5)–C(6)–C(7)	178.3(15)
C(6)–C(7)–H(7)	177.8(20)	Re–C(8)–N(1)	116.7(7)
Re–C(8)–N(2)	126.7(8)	N(1)–C(8)–N(2)	116.4(9)

as CO-loss fragments. Complex **7** has also been crystallographically characterized. An ORTEP drawing is shown in Figure 3, and relevant crystallographic details are given in Tables 6 and 7. The structure parameters of **7** closely resemble those of the bromine analogue $\mathrm{ReBr(CO)_4\{C(NHPr^i)(NHPh)\}}$ (**1a**).[7] Pseudooctahedral geometry is also observed around the Re atom, with the dihedral angle of Cl–Re–C(5)–N(2) being −34.9(5)°. The C(5) atom of the diaminocarbene ligand appears as an sp^2 hybrid with a distorted-trigonal-planar arrangement. Both C(5)–N(1) and C(5)–N(2) bonds show partial double-bond character with distances of 1.316(18) and 1.349(17) Å, respectively. The Cl atom and the diaminocarbene group are *cis* to each other. The three CO ligands *cis* to the chlorine atom have slightly longer Re–C(CO) distances (1.993(16), 1.972(15), and 1.971(14) Å) than the *trans* CO group (1.914(16) Å). This is likely due to the inability of the Cl ligand to accept π electrons,[15] and this observation is similar to that for structure **6c**.

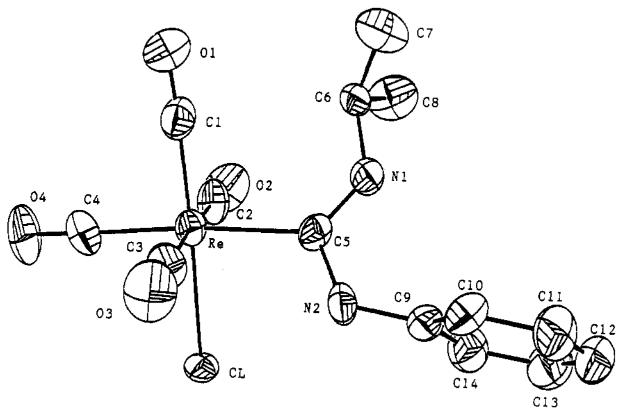

Figure 3. ORTEP diagram of $\mathrm{ReCl(CO)_4\{C(NHPr^i)(NHPh)\}}$ (**7**).

Table 6. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $\mathrm{ReCl(CO)_4\{C(NHPr^i)(NHPh)\}}$ (7)

atom	*x*	*y*	*z*	B_{iso}[a]
Re	0.26961(3)	0.12521(9)	0.24148(3)	2.764(24)
Cl	0.19163(22)	0.4321(5)	0.28126(19)	3.05(14)
N(1)	0.2923(7)	0.2765(19)	0.0728(7)	3.3(5)
N(2)	0.1644(7)	0.3797(21)	0.0947(6)	3.7(6)
O(1)	0.3598(8)	−0.2622(17)	0.2010(7)	5.6(6)
O(2)	0.4504(7)	0.3643(20)	0.3079(7)	6.2(6)
O(3)	0.0831(7)	−0.0840(19)	0.1766(7)	5.8(6)
O(4)	0.2984(7)	−0.0555(20)	0.4120(6)	6.0(6)
C(1)	0.3265(9)	−0.1142(25)	0.2145(8)	3.7(7)
C(2)	0.3851(10)	0.278(3)	0.2846(9)	4.2(8)
C(3)	0.1509(9)	−0.007(3)	0.1996(8)	3.6(7)
C(4)	0.2867(9)	0.009(3)	0.3497(9)	3.9(7)
C(5)	0.2425(8)	0.2749(21)	0.1214(8)	2.9(6)
C(6)	0.3815(8)	0.1840(23)	0.0861(8)	3.3(6)
C(7)	0.3774(10)	0.026(3)	0.0231(10)	5.5(9)
C(8)	0.4490(9)	0.347(3)	0.0883(11)	5.4(9)
C(9)	0.1345(8)	0.4911(23)	0.0207(8)	3.2(6)
C(10)	0.0809(9)	0.3954(24)	−0.0475(9)	3.7(7)
C(11)	0.0515(10)	0.501(3)	−0.1198(9)	4.4(8)
C(12)	0.0749(11)	0.701(3)	−0.1241(10)	4.8(9)
C(13)	0.1294(12)	0.800(3)	−0.0571(11)	5.1(9)
C(14)	0.1581(10)	0.695(3)	0.0166(10)	4.5(8)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 7. Selected Bond Distances and Angles for $\mathrm{ReCl(CO)_4\{C(NHPr^i)(NHPh)\}}$ (7)

(a) Bond Distances (Å)			
Re–Cl	2.534(3)	Re–C(1)	1.914(16)
Re–C(2)	1.993(16)	Re–C(3)	1.971(14)
Re–C(4)	1.972(15)	Re–C(5)	2.226(13)
N(1)–C(5)	1.316(18)	N(1)–C(6)	1.470(16)
N(2)–C(5)	1.349(17)	N(2)–C(9)	1.425(17)
O(1)–C(1)	1.147(19)	O(2)–C(2)	1.125(19)
O(3)–C(3)	1.127(17)	O(4)–C(4)	1.125(18)
(b) Bond Angles (deg)			
Cl–Re–C(1)	177.4(4)	Cl–Re–C(2)	88.1(5)
Cl–Re–C(3)	87.9(5)	Cl–Re–C(4)	88.3(5)
Cl–Re–C(5)	87.1(4)	C(1)–Re–C(2)	93.2(6)
C(1)–Re–C(3)	90.8(6)	C(1)–Re–C(4)	89.5(6)
C(1)–Re–C(5)	95.0(5)	C(2)–Re–C(3)	175.9(7)
C(2)–Re–C(4)	89.3(6)	C(2)–Re–C(5)	91.6(5)
C(3)–Re–C(4)	91.4(6)	C(3)–Re–C(5)	87.4(5)
C(4)–Re–C(5)	175.3(6)	N(2)–C(9)–C(10)	120.0(13)
C(5)–N(1)–C(6)	128.1(11)	N(2)–C(9)–C(14)	120.8(13)
C(5)–N(2)–C(9)	125.1(11)	Re–C(1)–O(1)	177.0(13)
Re–C(2)–O(2)	179.0(13)	Re–C(3)–O(3)	179.1(12)
Re–C(4)–O(4)	178.4(12)	Re–C(5)–N(1)	129.1(9)
Re–C(5)–N(2)	115.6(9)	N(1)–C(5)–N(2)	115.3(11)

The reactions of **2a** with Brønsted acids $\mathrm{RCO_2H}$ are believed to proceed initially via an electrophilic attack by the acid proton at the Re–C σ bond to yield the cationic intermediate $\mathrm{[Re(CO)_4\{C(NHPr^i)(NHPh)\}]^+}$ (**8**), followed by coordination of the carboxylate anion to give the addition product **6**.[16] The cationic intermediate **8** is probably chlorinated by either $\mathrm{CH_2Cl_2}$ solvent or HCl present in the chlorinated solvent[17] to generate complex **7**. The reaction rate of complex **2a** with Brønsted acids at room temperature decreases in the order $\mathrm{CF_3CO_2H}$ > $\mathrm{CH{\equiv}CCO_2H}$ > $\mathrm{CH_3CO_2H}$, with the completion time ranging between 1 min and 25 h to afford **6**. These results indicate that complex **6** is formed by a mechanism involving the initial protonation of complex **2** rather than by direct oxidative addition of HX, since the stronger the acid, the faster the reaction. Lewis and co-workers have investigated the reaction of Brønsted acids (HX) with the cyclometalated cluster $\mathrm{Os_3H_2(CO)_9\{P(C_6H_4)Ph\}}$ to give the addition product $\mathrm{Os_3H_2X(CO)_9(PPh_2)}$.[16] They found that acetic acid alone has insufficient strength to react with the cyclometalated complex, and the product $\mathrm{Os_3H_2(CH_3CO_2)(CO)_9(PPh_2)}$ could not be isolated due to its insta-

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(16) Colbran, S. B.; Irele, P. T.; Johnson, B. F. G.; Kaye, P. T.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2033.

(17) (a) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (b) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Organometallics* **1992**, *11*, 853.

bility. In our observations, the cyclometalated rhenium complex **2a** shows good reactivity toward acetic acid and the product $Re(CO)_4(\eta^1-OCOCH_3)\{C(NHPr^i)(NHPh)\}$ (**6a**) is air stable.

Concluding Remarks. In comparison to other extensively studied cyclometalated ligands with N and P as the donor atoms, it is rare to observe ortho metalation occurring in (diaminocarbene)metal complexes.[3,4,17] Although both the diaminocarbene complex **1** and the cyclometalated product **2a** are stable in air in the solid state, the closing and opening of the Re–C σ bond in solution is facile, reversible, and successive and occurs under very mild reaction conditions. It is well-known that the employment of "activated" complexes which are coordinatively unsaturated or in which the carbonyl ligands have been partially replaced by more labile donors provides a useful precursor to incorporate ligands of interest into metal complexes. The reactive Re–C σ bond of the cyclometalated diaminocarbene complexes is demonstrated by its facile electrophilic addition of HBr, RCO_2H, and I_2 at room temperature, and it could be exploited to prepare a series of rhenium diaminocarbene derivatives. Due to this special reaction pathway, we were able to prepare the unusual 2,6-diiodo-1-aminophenyl group in the rhenium complex.

Experimental Section

General Data. The complexes $ReBr(CO)_4\{C(NHPr^i)(NHPh)\}$ and $ReBr(CO)_4\{C(NHPr)(NHPh)\}$ were prepared previously.[7] Other reagents were purchased from commercial sources and were used as received. All manipulations were performed with standard Schlenk techniques. Chromatographic separations could be done in air if exposure is limited to a few hours. Solvents were dried by stirring over Na/benzophenone (diethyl ether) or CaH_2 (hexane, CH_2Cl_2) and were freshly distilled prior to use. IR spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Bruker MSL-200, AC-200, or AMX-500 FT NMR spectrometer, and mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer.

Synthesis of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_4)\}$ (2a). A solution of $ReBr(CO)_4\{C(NHPr^i)(NHPh)\}$ (500 mg, 0.93 mmol) in CH_2Cl_2 (300 mL) and Et_2NH (10 mL) was stirred for 45 h at room temperature. The solvent was removed under vacuum, and the solid was extracted with diethyl ether (2 × 100 mL). The residue was recrystallized from CH_2Cl_2/hexane to give $Et_2NH_2^+Br^-$. The extracts were chromatographed on a silica gel TLC plate with 30:100 CH_2Cl_2/hexane as eluent to give $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_4)\}$ (**2a**; 264 mg, 0.57 mmol, 62%). Anal. Calcd for $C_{14}H_{13}N_2O_4Re$: C, 36.53; H, 2.82. Found: C, 36.60; H, 2.89. IR (CH_2Cl_2): ν_{CO} 2081 (m), 1979 (vs), 1916 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.96 (br, 1 H, NHC_6H_4), 7.69, 6.96, 6.80 (m, 1 H, 1 H, 2 H, respectively, C_6H_4), 6.01 (d, br, 1 H, $NHPr^i$), 3.80 (m, 1 H, CH), 1.30 (d, 6 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 197.60, 193.11, 192.29, 188.32 (C (diaminocarbene) and CO ligands), 154.53 (C–Re, Ph), 138.73 (C–N, Ph), 143.22, 124.06, 123.57, 110.84 (Ph), 44.83 (CH), 22.58 (2 CH_3). MS (EI, Re^{187}): *m/z* 460 (M^+), 432 ($M^+ - CO$), 404 ($M^+ - 2CO$), 376 ($M^+ - 3CO$), 348 ($M^+ - 4CO$). ^1H NMR for $Et_2NH_2^+Br^-$ ($CDCl_3$): δ 9.30 (br, NH_2), 2.99 (q, 4 H, CH_2), 1.43 (t, 6 H, CH_3).

Synthesis of $Re(CO)_4\{\eta^2-C(NHPr)(NHC_6H_4)\}$ (2b). A solution of $ReBr(CO)_4\{C(NHPr)(NHPh)\}$ (190 mg, 0.35 mmol) in CH_2Cl_2 (100 mL) and Et_2NH (10 mL) was stirred for 3 days at room temperature. The solvent was removed under vacuum, and the residue was extracted with diethyl ether (2 × 100 mL) and chromatographed on a silica gel TLC plate with 30:100 CH_2Cl_2/hexane as eluent to give $Re(CO)_4\{\eta^2-C(NHPr)(NHC_6H_4)\}$ (**2b**; 49 mg, 0.11 mmol, 31%). IR (CH_2Cl_2): ν_{CO} 2081 (m), 1978 (vs), 1915 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.02 (br, 1 H, NHC_6H_4), 7.76, 7.02, 6.86 (m, 1 H, 1 H, 2 H, respectively, C_6H_4), 6.15 (br, 1 H, $NHPr$), 3.26 (m, 2 H, CH_2), 1.77 (m, 2 H, CH_2), 1.07 (t, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 198.77, 193.11, 192.24, 188.28 (C (diaminocarbene) and CO ligands), 154.43 (C–Re, Ph), 138.72 (C–N, Ph), 143.23, 124.07, 123.61, 110.89 (Ph), 44.60 ($NHCH_2$), 21.91 (CH_2CH_3), 11.33 (CH_3). MS (EI, Re^{187}): *m/z* 460 (M^+), 432 ($M^+ - CO$), 404 ($M^+ - 2CO$), 376 ($M^+ - 3CO$).

Reaction of $Re(CO)_4\{\eta^2-C(NHR)(NHC_6H_4)\}$ (2) with HBr. Hydrogen bromide gas was bubbled through a solution of complex **2a** or **2b** in CH_2Cl_2 at room temperature until the pattern of the carbonyl bands of the reactant in the IR spectrum had completely changed; the IR data indicated that complex **1a** or **1b** was generated almost quantitatively. Stirring complex **2a** or **2b** with small amounts (0.1–0.5 mL) of aqueous HBr in CH_2Cl_2 solution at room temperature gave similar results.

Reaction of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_4)\}$ (2a) with Iodine. A solution of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_4)\}$ (**2a**; 202 mg, 0.44 mmol) in CH_2Cl_2 (50 mL) was treated with a solution of I_2 (148 mg, 0.58 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 30:100 CH_2Cl_2/hexane as eluent to give $ReI(CO)_4\{C(NHPr^i)(NHC_6H_4I)\}$ (**3**; 226 mg, 0.32 mmol, 72%). Anal. Calcd for $C_{14}H_{13}I_2N_2O_4Re$: C, 23.57; H, 1.84. Found: C, 23.73; H, 1.67. IR (CH_2Cl_2): ν_{CO} 2100 (m), 2000 (vs), 1932 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.36 (br, 1 H, NHC_6H_4I), 7.96, 7.90 (dd, 1 H, C_6H_4I, two isomers, δ 7.90 is overlapped with the absorption of $NHPr^i$, characterized by homonuclear COSY 2D spectrum), 7.43, 7.18 (m, 1 H, 2 H, respectively, C_6H_4I), 7.90, 5.70 (d, br, 1 H, $NHPr^i$, two isomers), 4.29, 3.86 (m, 1 H, CH, two isomers in a 10:3 ratio), 1.42, 1.21 (d, 6 H, CH_3, two isomers in a 3:10 ratio). ^1H NMR (C_6D_6): δ 8.39, 6.44 (br, 1 H, NHC_6H_4I, two isomers), 7.51, 7.41 (dd, 1 H, C_6H_4I, two isomers in an 8:10 ratio), 6.90, 6.53 (m, 1 H, 2 H, respectively, C_6H_4I), 8.08, 5.37 (d, br, 1 H, $NHPr^i$, two isomers in an 8:10 ratio), 4.13, 2.79 (m, 1 H, CH, isomers in a 10:8 ratio), 0.81, 0.66 (d, 6 H, CH_3, two isomers in an 8:10 ratio).

Preparation of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_3I)\}$ (4). A solution of $ReI(CO)_4\{C(NHPr^i)(NHC_6H_4I)\}$ (86 mg, 0.12 mmol) in CH_2Cl_2 (400 mL) and Et_2NH (10 mL) was stirred for 3 days at room temperature. The solvent was removed under vacuum, and the residue was extracted with diethyl ether (2 × 50 mL) and chromatographed on a silica gel TLC plate with 30:100 CH_2Cl_2/hexane as eluent to give $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_3I)\}$ (**4**; 34 mg, 0.06 mmol, 48%). Anal. Calcd for $C_{14}H_{12}IN_2O_4Re$: C, 28.73; H, 2.07. Found: C, 28.74; H, 1.38. IR (CH_2Cl_2): ν_{CO} 2084 (m), 1981 (vs), 1920 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.49 (br, 1 H, NHC_6H_3I), 7.62 (dd, 1 H, C_6H_3), 7.32 (dd, 1 H, C_6H_3), 6.52 (t, 1 H, C_6H_3), 6.14 (d, br, 1 H, $NHPr^i$), 3.90 (m, 1 H, CH), 1.41 (d, 6 H, CH_3).

Reaction of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_3I)\}$ (4) with Iodine. A solution of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_3I)\}$ (**4**; 145 mg, 0.25 mmol) in CH_2Cl_2 (50 mL) was treated with a solution of I_2 (90 mg, 0.35 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 2 days at room temperature. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 30:100 CH_2Cl_2/hexane as eluent to give $ReI(CO)_4\{C(NHPr^i)(NHC_6H_3I_2)\}$ (**5**; 79 mg, 0.09 mmol, 38%). Anal. Calcd for $C_{14}H_{12}I_3N_2O_4Re$: C, 20.04; H, 1.44. Found: C, 20.20; H, 1.16. IR (CH_2Cl_2): ν_{CO} 2100 (m), 2000 (vs), 1928 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.51 (br, 1 H, $NHC_6H_3I_2$), 7.95, 7.93 (d, 2 H, $C_6H_3I_2$, two isomers in a 20:1 ratio), 6.79 (t, 1 H, $C_6H_3I_2$), 5.58 (d, br, 1 H, $NHPr^i$), 4.36, 3.92 (m, 1 H, CH, two isomers in a 20:1 ratio), 1.47, 1.25 (d, 6 H, CH_3, two isomers in a 1:20 ratio). MS (FAB, Re^{187}): *m/z* 840 (M^+), 812 ($M^+ - CO$), 756 ($M^+ - 3CO$), 728 ($M^+ - 4CO$), 713 ($M^+ - I$), 685 ($M^+ - I - CO$), 657 ($M^+ - I - 2CO$).

Reaction of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_4)\}$ (2a) with CH_3CO_2H. A solution of $Re(CO)_4\{\eta^2-C(NHPr^i)(NHC_6H_4)$ (**2a**; 200 mg, 0.44 mmol) in CH_2Cl_2 (130 mL) was treated with excess CH_3CO_2H (2 mL). The mixture was stirred for 25 h at room temperature. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 70:

100 CH_2Cl_2/hexane as eluent to give $Re(CO)_4(\eta^1\text{-}OCOCH_3)\{C(NHPr^i)(NHPh)\}$ (**6a**; 124 mg, 0.24 mmol, 55%). Anal. Calcd for $C_{14}H_{13}I_2N_2O_4Re$: C, 23.57; H, 1.84. Found: C, 23.73; H, 1.67. IR (CH_2Cl_2): ν_{CO} 2107 (m), 2002 (vs), 1935 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.37, 8.00 (s, br, 1 H, N*H*Ph, two isomers in a 6:1 ratio), 7.50–7.07 (m, 5 H, Ph), 8.15, 6.33 (d, br, 1 H, N*H*Pr^i, two isomers in a 1:6 ratio), 4.22, 3.84 (m, 1 H, CH, two isomers in a 6:1 ratio), 2.05 (s, 3 H, H_3CCO_2), 1.29, 1.20 (d, 6 H, CH_3, two isomers in a 1:6 ratio).

Reaction of $Re(CO)_4\{\eta^2\text{-}C(NHPr^i)(NHC_6H_4)\}$ (2a) with CF_3CO_2H. A solution of $Re(CO)_4\{\eta^2\text{-}C(NHPr^i)(NHC_6H_4)\}$ (**2a**; 128 mg, 0.28 mmol) in CH_2Cl_2 (100 mL) was treated with excess CF_3CO_2H (0.1 mL). The mixture was stirred for 5 min at room temperature. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 50:100 CH_2Cl_2/hexane as eluent to give $Re(CO)_4(\eta^1\text{-}OCOCF_3)\{C(NHPr^i)(NHPh)\}$ (**6b**; 102 mg, 0.18 mmol, 63%). IR (CH_2Cl_2): ν_{CO} 2108 (m), 2001 (vs), 1937 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.69, 7.97 (s, br, 1 H, N*H*Ph, two isomers in a 3:1 ratio), 7.52–7.07 (m, 5 H, Ph), 7.77, 6.48 (d, br, 1 H, N*H*Pr^i, two isomers in a 1:3 ratio), 4.19, 3.88 (m, 1 H, CH, two isomers in a 3:1 ratio), 1.30, 1.23 (d, 6 H, CH_3, two isomers in a 1:3 ratio). MS (EI, Re^{187}): *m/z* 574 (M^+), 546 ($M^+ - CO$), 518 ($M^+ - 2CO$), 462 ($M^+ - 4CO$).

Reaction of $Re(CO)_4\{\eta^2\text{-}C(NHPr^i)(NHC_6H_4)\}$ (2a) with Propynoic Acid. A solution of $Re(CO)_4\{\eta^2\text{-}C(NHPr^i)(NHC_6H_4)\}$ (**2a**; 300 mg, 0.65 mmol) in CH_2Cl_2 (250 mL) was treated with excess $HC\equiv CCO_2H$ (0.5 mL). The mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 70:100 CH_2Cl_2/hexane as eluent to give $Re(CO)_4(\eta^1\text{-}OCOC\equiv CH)\{C(NHPr^i)(NHPh)\}$ (**6c**; 204 mg, 0.39 mmol, 59%) and $ReCl(CO)_4\{C(NHPr^i)(NHPh)\}$ (**7**; 26 mg, 0.05 mmol, 8%). **6c**: Anal. Calcd for $C_{17}H_{15}N_2O_6Re$: C, 38.55; H, 2.83. Found: C, 38.41; H, 2.81. IR (CH_2Cl_2): ν_{CO} 2105 (m), 1998 (vs), 1928 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.03, 7.82 (s, br, 1 H, N*H*Ph, two isomers in a 4:1 ratio), 7.52–7.10 (m, 5 H, Ph), 8.03, 6.37 (d, br, 1 H, N*H*Pr^i, two isomers in a 1:4 ratio), 4.20, 3.82 (m, 1 H, CH, two isomers in a 4:1 ratio), 2.62 (s, 1 H, $HC\equiv C$), 1.36, 1.21 (d, 6 H, CH_3, two isomers in a 1:4 ratio). MS (EI, Re^{187}): *m/z* 530 (M^+), 502 ($M^+ - CO$), 461 ($M^+ - HC\equiv CCO_2$), 433 ($M^+ - HC\equiv CCO_2 - CO$), 405 ($M^+ - HC\equiv CCO_2 - 2CO$), 377 ($M^+ - HC\equiv CCO_2 - 3CO$), 349 ($M^+ - HC\equiv CCO_2 - 4CO$). **7**: Anal. Calcd for $C_{14}H_{14}ClN_2O_4Re$: C, 33.89; H, 2.82. Found: C, 33.25; H, 2.57. IR (CH_2Cl_2): ν_{CO} 2105 (m), 2000 (vs), 1926 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.68, 9.16 (s, br, 1 H, N*H*Ph, two isomers in a 10:1 ratio), 7.52–7.13 (m, 5 H, Ph), 8.32, 6.38 (d, br, 1 H, N*H*Pr^i, two isomers in a 1:10 ratio), 4.25, 3.80 (m, 1 H, CH, two isomers in a 10:1 ratio), 1.32, 1.21 (d, 6 H, CH_3, two isomers in a 1:10 ratio). MS (EI, Re^{187}, Cl^{35}): *m/z* 496 (M^+), 468 ($M^+ - CO$), 440 ($M^+ - 2CO$), 412 ($M^+ - 3CO$).

^1H NMR Data for $ReBr(CO)_4\{C(NHR)(NHPh)\}$ (1a, R = Pr^i; 1b, R = Pr). Complexes $ReBr(CO)_4\{C(NHPr^i)(NHPh)\}$ (**1a**) and $ReBr(CO)_4\{C(NHPr)(NHPh)\}$ (**1b**) were prepared previously.[7] Both **1a** and **1b** exist as two isomeric forms in solution. **1a**: ^1H NMR ($CDCl_3$): δ 8.82, 7.75 (s, 1 H, N*H*Ph, two isomers in a 7:1 ratio), 7.52–7.28 (m, 5 H, Ph), 8.01, 6.35 (d, 1 H, N*H*Pr^i, two isomers in a 1:7 ratio), 4.27, 3.82 (m, 1 H, CH, two isomers in a 7:1 ratio), 1.33, 1.21 (d, 6 H, CH_3, two isomers in a 1:7 ratio). **1b**: ^1H NMR ($CDCl_3$): δ 8.95, 7.72 (s, 1 H, N*H*Ph, two isomers in a 4:1 ratio), 7.51–7.39, 7.20–7.16 (m, 5 H, Ph), 8.04, 6.53 (br, 1 H, NH, two isomers in a 1:4 ratio), 3.52, 3.16 (m, 2 H, NHC*H*$_2$), 1.78, 1.56 (m, 2 H, C*H*$_2$CH$_3$, two isomers in a 1:4 ratio), 1.05, 0.90 (t, 3 H, CH_3, two isomers in a 1:4 ratio).

Crystallographic Structure Determination. Crystals of $ReI(CO)_4\{C(NHPr^i)(NHC_6H_4I)\}$ (**3**), $Re(CO)_4(\eta^1\text{-}OCOC\equiv CH)\{C(NHPr^i)(NHPh)\}$ (**6c**), and $ReCl(CO)_4\{C(NHPr^i)(NHPh)]$ (**7**) were grown from CH_2Cl_2/hexane solutions at −5 °C. Specimens of suitable quality were mounted on a glass capillary and used for measurement of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.709 30 Å) with θ–2θ scan mode for **6c** and **7**. Diffraction measurements were made on a Rigaku AFC5R diffractometer using graphite-monochromatized Cu Kα radiation (λ = 1.540 56 Å) with θ–2θ scan mode for **3**. Unit cells were determined and refined using 25 randomly selected reflections obtained with the automatic search, center, index, and least-squares routines. Space groups were determined from the systematic absences observed during data collection. The systematic absences in the diffraction data for **3**, **6c**, and **7** unambiguously established the space groups as *Pbcn*, *P*2$_1$/*n*, and *P*2$_1$/*c*, respectively. An empirical absorption correction was applied to each of the data sets. The structures were solved by heavy-atom methods. All remaining non-hydrogen atoms were located from the difference Fourier map, and they were included in the final refinement cycle and refined by full-matrix least squares. All of the data processing was carried out on a Microvax 3600 using the NRCC SDP program.[18]

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Supplementary Material Available: For **3**, **6c**, and **7**, tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles (12 pages). Ordering information is given on any current masthead page.

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[18] Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3; Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M.; Krueger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174.