Binuclear Metallapyrrolidone Complexes Formed from Coupling of CO and Alkynes with the μ_3-Nitrene Ligand of $Ru_3(\mu_3\text{-NPh})(CO)_{10}$

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Received March 12, 1987

The μ_3-nitrene cluster $Ru_3(CO)_{10}(\mu_3\text{-NPh})$ (**1**) reacts with $PhC{\equiv}CPh$ and $MeC{\equiv}CPh$ to give the binuclear metallapyrrolidone complexes $Ru_2(CO)_6(\mu_2\text{-}\eta^3\text{-PhC}{=}CRC(O)NPh)$ (**2**, R = Ph; **5**, R = Me) which form by combination of the alkyne with CO and the nitrene ligand. Minor products from the reactions are metallacyclopentadiene complexes, $Ru_2(C_4R_2Ph_2)(CO)_6$, $Ru_4(CO)_{11}(\mu_4\text{-NPh})(MeC{\equiv}CPh)$, and the unusual Ru_5 cluster $Ru_2(\mu_2\text{-}\eta^3\text{-PhC}{=}CPhC(O)NPh)(CO)_5\cdot Ru_3(\mu_3\text{-NPh})(CO)_6(\mu_3\text{-CO})$ (**3**). The structures of **2**, **3**, and **5** have been crystallographically established. **2**: monoclinic, $P2_1/c$, $a = 21.492$ (5) Å, $b = 7.840$ (1) Å, $c = 15.819$ (4) Å, $\beta = 100.6$ (2)°, $V = 2619.4$ (9) Å^3, $Z = 4$, R = 0.030, $R_w = 0.035$ from 4417 reflections with $F_o \geqslant 3\sigma(F_o)$. **3**: monoclinic, $P2_1/c$, $a = 15.315$ (5) Å, $b = 27.319$ (10) Å, $c = 20.593$ (7) Å, $\beta = 102.46$ (3)°, $V = 8412$ (7) Å^3, $Z = 4$, $R = 0.059$, $R_w = 0.058$ for the 5783 reflections with $F_o \geqslant 3\sigma(F_o)$. **5**: monoclinic, $P2_1/c$, $a = 7.732$ (1) Å, $b = 30.670$ (7) Å, $c = 19.432$ (4) Å, $\beta = 99.96°$, $V = 4538$ (2) Å^3, $Z = 4$, $R = 0.035$, $R_w = 0.038$ for 5061 reflections with $F_o \geqslant 4\sigma(F_o)$. Complexes **2** and **5** have a $\mu_2\text{-}\eta^3\text{-PhC}{=}C(R){-}C(O){-}NPh$ ligand bridging between the Ru atoms which are joined by a metal–metal bond. Each Ru is further ligated by three CO's. Compound **3** derives from combination of **1** with **2**. It has the μ_3-CO ligand of **1** bound to one Ru atom of **2** in an isocarbonyl fashion and one Ph ring of the $\mu_2\text{-}\eta^3\text{-PhC}{=}C(Ph){-}C(O){-}NPh$ ligand having replaced three CO's on a single Ru atom of **1**. Complex **3** was also directly prepared from the combination of **1** with **2** in refluxing cyclohexane. The diruthenium complex **2** further reacts with $PhC{\equiv}CPh$ to form pentaphenylpyridinone and $Ru_3(PhC{\equiv}CPh)_2(CO)_8$ (**10**). Complex **2** also reacts with CO upon photolysis to form 1,3,4-triphenylmaleimide.

Introduction

The chemistry of nitrene (NR, imido) ligands attached to electron-rich metals has been little developed, although much is known about the chemistry of such ligands bound to electron-deficient metals.[1] In the latter complexes, the nitrene ligand is typically attached to a single metal, in either a linear or bent coordination mode. Complexes containing doubly bridging μ_2-NR ligands are also known.[1] However, in low-valent, electron-rich complexes these coordination modes are unknown, and instead the nitrene ligand typically occupies a μ_3-triply bridging position in metal cluster compounds.[1,2-9] Relatively few studies of the chemistry of this class of compounds have been conducted, and the reactivity properties of μ_3-NR ligands are not well-understood, even though such ligands have been invoked as key intermediates in certain catalytic processes.[3c,5b,6a,9f,10]

We have begun to explore the chemistry of clusters that possess capping μ_3-NR ligands in order to develop the fundamental chemistry of this ligand and to determine its role in catalytic nitroarene carbonylation reactions.[8] In other work, we have shown that these ligands enhance cluster stability and permit the synthesis of formyl, acyl, and carbene derivatives of Fe_3 clusters that would otherwise be unstable in the absence of the capping μ_3-NPh ligands.[8a,b] That work also led to the conclusion that within this family of complexes the μ_3-NPh ligands are relatively more inert than are the corresponding μ_3-PPh ligands. Even so, methods were found for inducing the capping nitrene ligands to participate in chemical transformations, and coupling of the nitrene ligands with carbene, acyl, and

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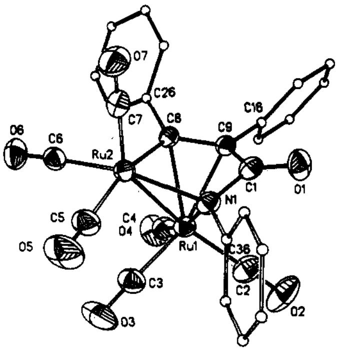
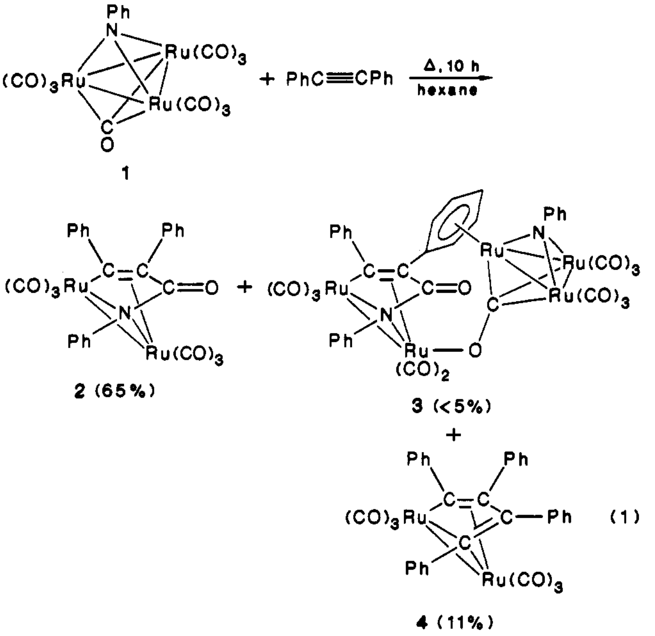


Figure 1. An ORTEP drawing of $Ru_2(CO)_6(\mu_2\text{-}\eta^3\text{-}PhC{=}C(Ph)C(O)NPh)$ (2). Thermal ellipsoids are drawn at the 40% probability level.

methoxycarbonyl ligands was observed.[8a,b] In our continuing study of the chemistry of this family of compounds, we have explored the reactions of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ with alkynes, and those results are reported herein. A preliminary report of part of this work has appeared.[8c]

Results

Reaction of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ with PhC≡CPh. Three products form when $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ (1) is heated in the presence of PhC≡CPh (eq 1). The predominant product is the binuclear complex 2 which contains a bridging acrylamide ligand as part of metallapyrrolidone ring. This species has been crystallographically characterized (Figure 1), and its spectroscopic data are consistent with its formulation. Spectroscopic data for all new complexes reported herein are given in the Experimental section. For 2, particularly significant is the 1717 cm^{-1} ν(CO) stretch for the acrylamide carbonyl which the structure shows not to be bound to either metal atom.



(1)

Complex 3 is a combination of 2 and the parent complex 1 linked together by an isocarbonyl ligand from 1 and an η^6-phenyl group from 2. This species has been crystallographically characterized (Figure 2). Its IR spectrum shows two weak bands at 1736 and 1691 cm^{-1} due to the isocarbonyl ligand and the uncomplexed acrylamide carbonyl, but these cannot be distinguished. Although complex 3 only forms in trace quantities in the reaction of 1 with PhC≡CPh, it can be prepared in 49% yield from the direct reaction of isolated 2 with 1. Although a few other compounds are known which have μ_4-isocarbonyl ligands similar to that in 3 (cf. $Cp_2M(OCCo(CO)_9)_2$, M = Zr, Hf),[11] compound 3 is the first example with such a ligand bound only to late transition metals.

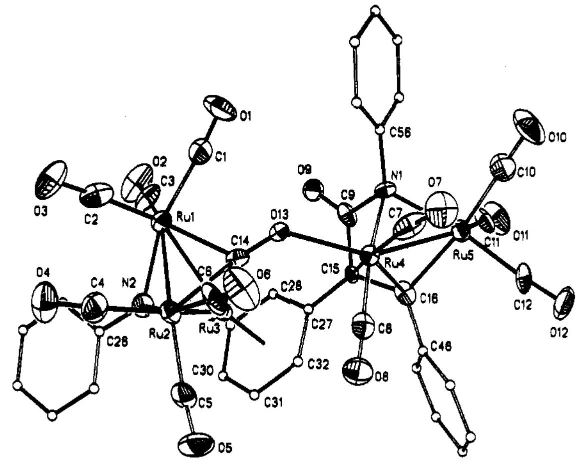


Figure 2. An ORTEP drawing of molecule A of $Ru_2(\mu_2\text{-}\eta^3\text{-}PhC{=}CPhC(O)NPh)(CO)_5{\cdot}Ru_3(\mu_3\text{-}NPh)(CO)_6(\mu_3\text{-}CO)$ (3). Thermal ellipsoids are drawn at the 40% probability level.

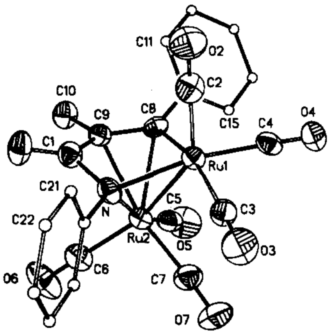
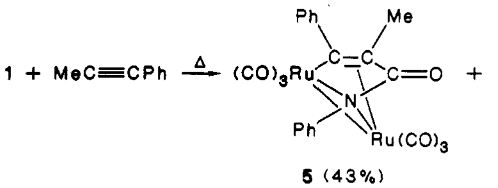


Figure 3. An ORTEP drawing of molecule A of $Ru_2(CO)_6(\mu_2\text{-}\eta^3\text{-}PhC{=}C(Me)C(O)NPh)$ (5). Thermal ellipsoids are drawn at the 40% probability level.

The third product of this reaction is the known binuclear complex 4 whose spectroscopic data confirm its identity.[12] This species was previously prepared from the reaction of $Ru_3(CO)_{12}$ with PhC≡CPh,[12] and it may form in our reaction through the interaction of PhC≡CPh with Ru carbonyl fragments generated in the 1 to 2 conversion.

Reaction of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ with PhC≡CMe. The predominant product of the thermal reaction of 1 with PhC≡CMe is binuclear 5 with a bridging acrylamide ligand similar to that found in complex 2 (eq 2). Complex



$Ru_4(\mu_4\text{-}NPh)(CO)_{11}(MeC{\equiv}CPh)$ + $Ru_2(CO)_6(\mu_2\text{-}\eta^4\text{-}Ph_2Me_2C_4)$

6 (11%) 7 (4%) (2)

5 has been crystallographically characterized (Figure 3), and its structure is similar to that of 2 with the phenyl substituent of the acrylamide ligand attached to the carbon

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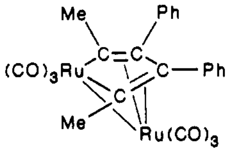
Table I. Crystallographic Data for $Ru_2(CO)_6(PhC{=}C(Ph)C(O)NPh)$ (2), $Ru_2(\mu_2\text{-}PhC{=}CPhC(O)NPh)(CO)_5 \bullet Ru_3(\mu_3\text{-}NPh)(CO)_6(\mu_3\text{-}CO)$ (3), and $Ru_2(CO)_6(PhC{=}C(Me)C(O)NPh)$ (5)

	2	3	5
(a) Crystal Parameters			
formula	$C_{27}H_{15}NO_7Ru_2$	$C_{39}H_{20}N_2O_{13}Ru_5$	$C_{22}H_{13}NO_7Ru_2$
mol wt	667.5	1229.9	605.5
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	21.492 (5)	15.315 (5)	7.732 (1)
b, Å	7.840 (1)	27.319 (10)	30.670 (7)
c, Å	15.819 (4)	20.593 (7)	19.432 (4)
β, deg	100.6 (2)	102.46 (3)	99.96 (2)
V, Å^3	2619 (9)	8412 (7)	4538 (2)
Z	4	8	8
μ, cm^{-1}	17.4	17.9	13.4
ρ, g cm^{-3} (calcd)	1.693	1.942	1.772
size, mm	0.23 × 0.31 × 0.32	0.31 × 0.32 × 0.34	0.34 × 0.34 × 0.34
color	yellow	deep red	yellow
(b) Data Collection			
diffractometer	Nicolet R3		
radiation	Mo Kα (λ = 0.71073 Å)		
monochromator	graphite		
2*θ* scan range, deg	$4 \le 2\theta \le 53$	$4 \le 2\theta \le 42$	$4 \le 2\theta \le 50$
scan type	Wyckoff	omega	omega
scan spd, deg min^{-1}	var 5–20	var 5–20	var 4–20
temp, °C	293	293	293
std rflns		3 std/197 rflns	
T_{max}/T_{min}	0.436/0.393	0.722/0.640	0.611/0.504
(c) Data Reduction and Refinement			
rflns collected	6042	10590	8543
unique rflns	5416	9025	7563
R(int), %	1.67	1.08	0.94
unique rflns with $F_o \ge n\sigma(F_o)$	4417 (*n* = 3)	5783 (*n* = 3)	5337 (*n* = 4)
R_F,^{a} %	2.99	5.92	3.50
R_{wF},^{a} % (*g* = 0.001)	3.53	5.78	3.83
highest peak, final diff Fourier, e Å^{-3}	0.46	0.96	0.76
N_o/N_v	14.8	5.9	9.5

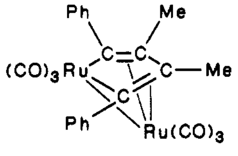
^{a} $w^{-1} = \sigma^2(F_o) + g(F_o^2)$; $R_F = \sum|\Delta|/\sum|F_o|$; $R_{wF} = \sum(|\Delta|w^{1/2})/\sum(|F_o|w^{1/2})$; $\Delta = |F_o| - |F_c|$.

adjacent to the ruthenium atom. This reaction is highly regioselective. The isomer of **5** with the Ph and Me substituents interchanged was formed in less than 2% yield. This latter species separated from **5** upon chromatography, and it showed IR and mass spectra identical with those of **5**.

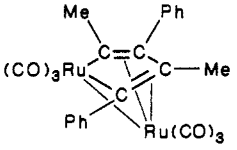
The second major product of reaction 2 is compound **6**. This species has been given the formulation $Ru_4(\mu_4\text{-}NPh)(CO)_{11}(MeC{\equiv}CPh)$ on the basis of the *m/z* 919 parent ion in its mass spectrum and the similarity of its IR spectrum to that reported for the analogous complex. $Ru_4(\mu_4\text{-}NH)(CO)_{11}(PhC{\equiv}CPh)$ which has been structurally characterized by Gladfelter et al.[4c] Also formed in low yield in reaction 2 is a mixture of stereoisomers of $Ru_2(CO)_6(\mu_2\text{-}\eta^4\text{-}Ph_2Me_2C_4)$ which apparently differ in the mode of coupling of the alkynes to form the metallacyclopentadiene ring, with possible structures illustrated in **7a–c**. These isomers do not separate upon chromatography but give IR and mass spectra consistent with the formulation of the complex. The ^1H NMR spectrum shows 3 singlets in the methyl region whose total intensity gives the expected 5:3 ratio with the phenyl protons, but there is no basis to specifically assign the individual resonances to any of the three isomers drawn above.



7a



7b



7c

In a subsequent experiment it was discovered that reaction 2 proceeds more cleanly to **5** if it is conducted under photochemical conditions in a quartz reaction vessel. Complex **5** was isolated in 85% yield from such reaction along with a small amount of a prsently unidentified compound. This is clearly the synthetic method of choice.

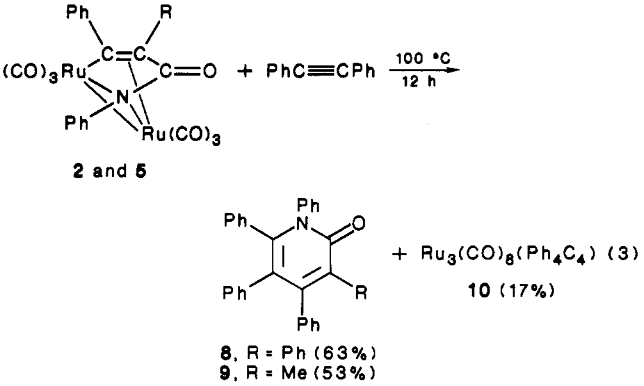
We presume that a trinuclear nitrene–alkyne complex is initially formed upon reaction of **1** with PhC≡CPh and PhC≡CMe but that this species rapidly fragments to give **2** and **5** under the reaction conditions. In an effort to prepare such a species under milder conditions, cluster **1** was treated with Me_3NO in CH_3CN at 22 °C. This gave immediate formation of a new compound with IR bands at 2087, 2056, 2033, 2014, and 1709 cm^{-1} which is presumably $Ru_3(\mu_3\text{-}NPh)(CO_9)(CH_3CN)$, in analogy to similar reactions with $Os_3(CO)_{12}$[13] and $Ru_3(CO)_{12}$.[14] In support

Table II. Selected Bond Distances and Angles for $Ru_2(CO)_6(PhC{=}C(R)C(O)NPh)$

2 (R = Ph)		5 (R = Me)			2 (R = Ph)		5 (R = Me)		
			molecule A	molecule B				molecule A	molecule B
(a) Bond Distances (Å)									
Ru(1)–Ru(2)	2.677 (1)	Ru(1)–Ru(2)	2.668 (1)	2.675 (1)	N(1)–C(1)	1.437 (5)	N–C(1)	1.431 (8)	1.423 (8)
Ru(1)–N(1)	2.164 (3)	Ru(2)–N	2.159 (4)	2.152 (4)	N(1)–C(36)	1.452 (4)	N–C(26)	1.442 (6)	1.438 (6)
Ru(1)–C(8)	2.299 (3)	Ru(2)–C(8)	2.268 (5)	2.295 (5)	O(1)–C(1)	1.211 (5)	O(1)–C(1)	1.220 (8)	1.205 (8)
Ru(1)–C(9)	2.296 (3)	Ru(2)–C(9)	2.272 (6)	2.266 (6)	C(8)–C(9)	1.425 (5)	C(8)–C(9)	1.402 (8)	1.444 (8)
Ru(2)–N(1)	2.136 (3)	Ru(1)–N	2.106 (5)	2.108 (5)	C(1)–C(9)	1.494 (5)	C(1)–C(9)	1.475 (8)	1.488 (8)
Ru(2)–C(8)	2.073 (3)	Ru(1)–C(8)	2.076 (6)	2.067 (6)					
(b) Bond Angles (deg)									
N(1)–Ru(1)–C(8)	71.1 (1)	N–Ru(2)–C(8)	71.4 (2)	77.1 (2)	N(1)–C(1)–C(9)	106.3 (3)	N–C(1)–C(9)	107.8 (5)	107.0 (5)
Ru(1)–N(1)–Ru(2)	77.0 (1)	Ru(1)–N–Ru(2)	77.4 (2)	77.8 (2)	O(1)–C(1)–C(9)	128.3 (4)	O(1)–C(1)–C(9)	127.4 (6)	126.3 (6)
Ru(1)–N(1)–C(1)	90.0 (2)	Ru(2)–N–C(1)	89.1 (3)	89.0 (3)	Ru(1)–C(8)–Ru(2)	75.3 (1)	Ru(1)–C(8)–Ru(2)	75.7 (2)	75.5 (2)
Ru(2)–N(1)–C(1)	114.4 (2)	Ru(1)–N–C(1)	113.0 (3)	114.5 (4)	Ru(2)–C(8)–C(9)	116.3 (2)	Ru(1)–C(8)–C(9)	116.3 (4)	115.0 (4)
N(1)–C(1)–O(1)	125.0 (3)	N–C(1)–O(1)	124.5 (5)	126.3 (5)	C(1)–C(9)–C(8)	114.7 (3)	C(1)–C(9)–C(8)	113.6 (5)	114.2 (5)

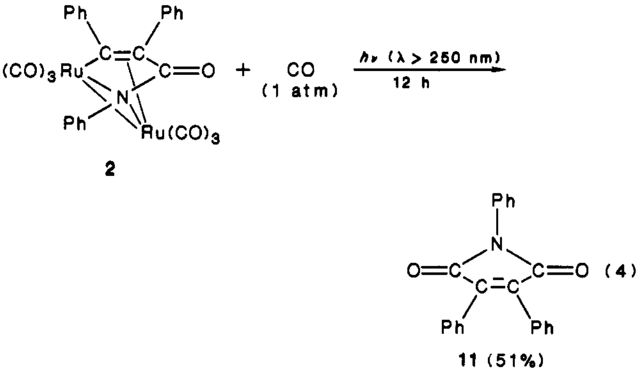
of this conclusion, it was noted that cluster **1** re-formed when the above solution was placed under a CO atmosphere. However, addition of $PhC\equiv CMe$ to the solution of $Ru_3(\mu_3\text{-}NPh)(CO)_9(CH_3CN)$ at 22 °C gave immediate formation of the metallapyrrolidone complex **5** in 32% yield, but with no evidence for a trinuclear nitrene–alkyne cluster.

Reaction of 2 and 5 with Additional Alkyne. The metallapyrrolidone complexes **2** and **5** react further with excess $PhC\equiv CPh$ to give the pyridinones **8** and **9** (eq 3).



Also formed in the reaction with **2** is the known trinuclear metallacyclopentadiene complex $Ru_3(CO)_8(Ph_4C_4)$ (**10**)[15] which presumably results from the reaction of excess alkyne with $Ru_x(CO)_y$ fragments formed upon eliminating the pyridinone. The exact substitution pattern around the pyridinone ring of **9** is not known with certainty, although that drawn in eq 3 is expected on the basis of the connectivity present in the precursor **5**.

Reaction of 2 with CO To Form 1,3,4-Triphenylmaleimide. The metallapyrrolidone complex **2** also reacts with CO upon photolysis to form 1,3,4-triphenylmaleimide (eq 4). The latter reaction proceeds efficiently only upon photolysis. Unreacted **2** is recovered in ~90% yield from the *thermal* reaction with CO (1200 psi, 120 °C, 48 h).



Crystal and Molecular Structures of 2 and 5. ORTEP drawings of these molecules are shown in Figure 1 and 3; crystallographic parameters are given in Tables I and II. Compound **5** crystallizes with two independent but structurally similar molecules in the unit cell. Molecule A with the unprimed atom labels is shown in Figure 3. Complexes **2** and **5** have similar structures differing only in the substituents on the β-carbons of the metallapyrrolidone rings (**2**, R = Ph; **5**, R = Me). The two Ru atoms in each are joined by a single metal–metal bond (**2**, 2.6767 (5) Å; **5**, 2.668 (1)/2.675 (1) Å) and are bridged by the $\mu_2\text{-}\eta^3\text{-}PhC{=}C(R)C(O)NPh$ ligand which derives from combination of the nitrene ligand with CO and the added alkyne. Each Ru atom is further coordinated by three CO ligands.

Of special interest are the structural features within the metallapyrrolidone rings of **2** and **5**. The parameters of these complexes are similar to those of $Cp_2Rh_2(\mu_2\text{-}\eta^3\text{-}CF_3C{=}C(CF_3)C(O)NPh)$[16] and $Fe_2(CO)_6(\mu_2\text{-}\eta^3\text{-}EtOC{=}C(Me)C(O)NNCPh_2)$,[17] the only other molecules with similar structures. The metallapyrrolidone ring system in each is essentially planar with the maximum deviations from planarity associated with C(1) (**2**, 0.230 Å; **5**, 0.235 and 0.227 Å). Also, in each complex the metallapyrrolidone carbonyl is not bonded to either metal atom whereas the nitrogen atom symmetrically bridges both metals. The carbons that originated in the added alkyne are bonded to the binuclear unit as a σ,π-vinyl ligand. The C(8)–C(9) distances within this ligand are 1.425 (5) Å and 1.402 (8)/1.444 (9) Å for **2** and **5**, respectively, typical of π-bonded olefin ligands and corresponding to a bond order of 1–2. Also, the C(8) carbon in each molecule is ~0.2 Å closer to the Ru atom to which it is σ-bonded than it is to the Ru to which it has a π-bond.

Crystal and Molecular Structure of 3. The complex crystallized with two independent but structurally similar molecules in the asymmetric unit. Molecule A with the unprimed atom labels is shown in Figure 2. Relevant structural details are given in Tables I and III. The molecule results from the combination of **1** with **2**. The phenyl substituent of the β-carbon of the metallapyrrolidone ring of **2** has replaced three carbonyls on a single Ru atom of **1**, and, in turn, the μ_3-CO ligand of **1** is bound in an isocarbonyl fashion to one of the Ru atoms of **2**, having replaced one carbonyl. The two parts of the molecule maintain their basic identities, and there is little change in their structural features. Particularly important is the μ_4-isocarbonyl ligand. The Ru(4)–O(13) bond distance of 2.23 (1) Å clearly indicates a bonding interaction. It is only slightly longer than typical Ru–O single bond distances of ~2.1 Å as found in $Ru_4(CO)_{10}(C{=}CH\text{-}i\text{-}Pr)(\mu_3\text{-}OH)(\mu_2\text{-}PPh_2)$ [$(Ru\text{-}O)_{av}$ = 2.15 Å[18]] and $[(\eta^6\text{-}C_6H_6)Ru(\mu_3\text{-}OH)]_4^{4+}$ [$(Ru\text{-}O)_{av}$ = 2.12 Å[19]]. The isocarbonyl C(4)–O(13) distance of 1.270 (19) Å has lengthened by 0.1 Å from the 1.17-Å average of the corresponding μ_3-CO bond distances in the two independent molecules of the parent cluster **1**.[5a] Likewise, the Ru–C distances to the μ_4-CO ligand in **3** average 2.13 Å compared to the 2.17 Å average in **1**.[5a]

A complex, $Ru_3(\mu\text{-}NPh)(CO)_7(\eta^6\text{-}C_6H_6)$, which is similar to the Ru_3 portion of **3** has recently been reported and structurally characterized.[5c] This species has an η^6-benzene bound to one of the three Ru atoms, and an important consequence of that bonding is a marked asymmetry in the Ru–C distances to the μ_3-CO ligand. The Ru–C_μ distance of 1.981 (12) Å to the Ru atom ligated by the benzene molecule was 0.364 Å shorter than the 2.345-Å average of the other two Ru–C_μ distances.[5c] A similar but less dramatic effect is apparent in **3** where the Ru(3)–C(14)

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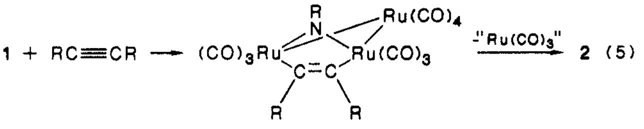
Table III. Selected Bond Distances and Angles for $Ru_2(\mu_2\text{-}\eta^3\text{-}PhC{=}CPhC(O)NPh)(CO)_5 \bullet Ru_3(\mu_3\text{-}NPh)(CO)_6(\mu_3\text{-}CO)$ (3)

	molecule A	molecule B
(a) Bond Distances (Å)		
Ru(1)–Ru(2)	2.742 (2)	2.753 (2)
Ru(1)–Ru(3)	2.734 (2)	2.716 (2)
Ru(2)–Ru(3)	2.699 (2)	2.717 (2)
Ru(4)–Ru(5)	2.675 (2)	2.662 (2)
Ru(1)–N(2)	2.074 (15)	2.065 (15)
Ru(2)–N(2)	2.066 (12)	2.044 (12)
Ru(3)–N(2)	2.021 (14)	2.035 (13)
Ru(4)–N(1)	2.188 (13)	2.196 (13)
Ru(5)–N(1)	2.103 (13)	2.165 (13)
Ru(1)–C(14)	2.184 (16)	2.174 (16)
Ru(2)–C(14)	2.213 (16)	2.200 (17)
Ru(3)–C(14)	1.984 (16)	1.996 (16)
Ru(3)–C(27)	2.284 (15)	2.256 (15)
Ru(3)–C(28)	2.249 (16)	2.275 (15)
Ru(3)–C(29)	2.267 (15)	2.249 (16)
Ru(3)–C(30)	2.307 (16)	2.263 (19)
Ru(3)–C(31)	2.274 (18)	2.255 (17)
Ru(3)–C(32)	2.240 (16)	2.212 (15)
Ru(4)–C(15)	2.260 (14)	2.302 (14)
Ru(4)–C(16)	2.236 (16)	2.275 (17)
Ru(4)–O(13)	2.234 (10)	2.239 (11)
Ru(5)–C(9)	2.085 (16)	2.050 (18)
N(1)–C(9)	1.409 (20)	1.402 (18)
O(9)–C(9)	1.219 (19)	1.217 (17)
O(13)–C(14)	1.270 (19)	1.244 (20)
C(9)–C(15)	1.489 (24)	1.476 (22)
C(15)–C(16)	1.434 (23)	1.416 (22)
(b) Bond Angles (deg)		
Ru(2)–Ru(1)–Ru(3)	59.1 (1)	59.6 (1)
Ru(1)–Ru(2)–Ru(3)	60.3 (1)	59.5 (1)
Ru(1)–Ru(3)–Ru(2)	60.6 (1)	60.9 (1)
Ru(2)–Ru(1)–C(14)	51.9 (4)	51.4 (4)
Ru(3)–Ru(1)–C(14)	45.9 (4)	46.4 (4)
Ru(1)–Ru(2)–C(14)	50.9 (4)	50.6 (4)
Ru(3)–Ru(2)–C(14)	46.4 (4)	46.4 (4)
Ru(1)–Ru(3)–C(14)	52.3 (5)	52.3 (5)
Ru(2)–Ru(3)–C(14)	53.8 (5)	53.0 (5)
Ru(5)–Ru(4)–O(13)	142.0 (3)	144.0 (3)
Ru(4)–N(1)–Ru(5)	77.1 (7)	75.2 (4)
Ru(1)–C(14)–Ru(2)	77.2 (5)	78.0 (6)
Ru(1)–C(14)–Ru(3)	81.8 (5)	81.2 (5)
Ru(2)–C(14)–Ru(3)	79.8 (6)	80.5 (6)
N(1)–Ru(5)–C(16)	76.3 (6)	76.1 (6)
N(1)–Ru(4)–O(13)	92.1 (4)	92.4 (4)
O(13)–Ru(4)–C(15)	87.1 (5)	88.0 (5)
O(13)–Ru(4)–C(16)	123.8 (5)	123.6 (5)
Ru(5)–N(1)–C(9)	115.1 (11)	114.7 (10)
Ru(1)–C(14)–O(13)	127.5 (12)	128.3 (13)
Ru(2)–C(14)–O(13)	128.3 (10)	129.3 (10)
Ru(3)–C(14)–O(13)	139.9 (12)	138.1 (13)
Ru(4)–O(13)–C(14)	128.0 (10)	128.2 (11)
Ru(4)–C(15)–C(27)	123.0 (10)	119.3 (10)
Ru(5)–C(16)–C(15)	114.9 (12)	117.4 (12)
N(1)–C(9)–O(9)	123.4 (15)	122.2 (14)
N(1)–C(9)–C(15)	106.6 (13)	109.4 (12)
O(9)–C(9)–C(15)	128.8 (15)	128.4 (14)
C(9)–C(15)–C(16)	114.4 (14)	115.2 (14)
C(9)–C(15)–C(27)	119.6 (13)	117.7 (13)
C(16)–C(15)–C(27)	124.9 (15)	127.0 (15)

distances of 1.984 (16) and 1.996 (16) Å for the two independent molecule of 3 average 0.25 Å less than the 2.24-Å average of the Ru–C(14) distances to the other two Ru atoms.

Discussion

There are several unique aspects of the research described herein. First is the coupling of the nitrene ligand with CO that occurs during the formation of the metallapyrrolidone complexes 2 and 5. In general, μ_3-nitrene ligands in clusters have proven remarkably resistant to carbonylation under quite severe conditions,[8b] and only under the effect of halide promotion has this reaction been found to occur.[20] However, nitrene–carbonyl coupling does occur in forming the metallapyrrolidone complexes 2 and 5. The mechanism by which these products form is unknown, but it is clear that the alkyne ligand must play an important role in this process. We tentatively suggest that a reactive nitrene complex such as **12** may be formed initially (eq 5) by analogy to the formation of similar compounds upon reaction of $Fe_3(\mu_3\text{-}PPh)(CO)_{10}$ with alkynes (see **14** in eq 6 below). A dibridging nitrene ligand should be much more reactive than a triply bridging nitrene, and nitrene–carbonyl coupling could readily occur in such a species to give the observed product **2**.



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Also interesting is the fact that the metallapyrrolidone ligands in 2 and 5 were generated by adding an alkyne to a preformed nitrene cluster, whereas the only other two examples of binuclear metallapyrrolidone complexes[16,17] were formed by the formal reverse order of reagent addition involving the reaction of nitrene sources with preformed alkyne complexes. The metallapyrrolidone ring system is obviously a thermodynamic sink in such chemistry, much like the binuclear metallacyclopentadiene ring systems formed in many reactions involving clusters and excess alkynes.[21]

Important features of the chemistry of the binuclear metallapyrrolidone complexes 2 and 5 are their reactions with added alkyne and CO to form the pyridinones 8 and 9 and the maleimide 11 (eq 3 and 4). Both of these transformations have precedent in the conversion of a mononuclear nickelapyrrolidone complex into these products[22] and in the use of Co and Ni complexes to catalyze the formation of pyridinones from alkynes and isocyanates.[23] The reactions given herein are the first demonstration of such chemistry from a binuclear metallapyrrolidone complex. Since the nitrene ligand in 1 initially derives from $PhNO_2$ or PhNO, we considered the possibility of catalyzing the formation of maleimides and pyridinones from $PhNO_2$, alkyne, and CO using $Ru_3(CO)_{12}$. However, when a 1:7:10 mixture of $Ru_3(CO)_{12}$, PhNO, and PhC≡CPh was heated to 100 °C for 12 h under 80 psi of CO, the bis(nitrene) cluster $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ was formed in near quantitative yield, but the alkyne was recovered unchanged.

It is interesting to compare the chemistry described herein to recently reported reactions of alkynes with the μ_3-phosphinidene iron analogue of 1, $Fe_3(\mu_3\text{-}PR)(CO)_{10}$, which gave the trinuclear products 13 and 14 (eq 6).[24] Similarly, reaction of the bis(phosphinidene) cluster $Fe_3(\mu_3\text{-}PPh)_2(CO)_9$ with alkynes under photochemical conditions led to addition of the alkyne across the bridging phosphorus centers (**15**), and thermal activation of these products induced their fragmentation to the binuclear

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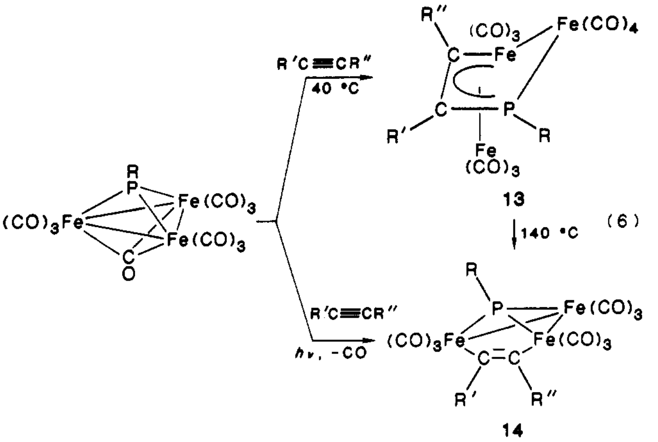
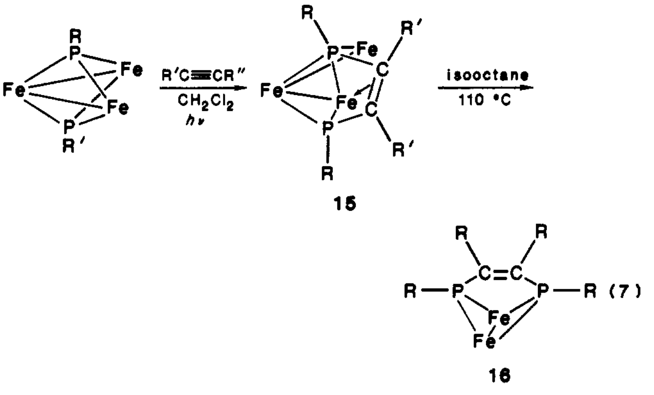


complexes 16 (eq 7).[25] The tetranuclear phosphinidene cluster $Fe_4(\mu_4\text{-PPh})_2(CO)_{11}$ also undergoes insertion of alkyne into the metal–phosphorus bonds,[26a] as does $Ru_4(\mu_4\text{-PPh})(CO)_{13}$.[26b]



R = R' = Ph; Fe ≡ $Fe(CO)_3$

It is clear from this and related studies[8] that μ_3-nitrene ligands in metal clusters can combine with a variety of other ligands including hydride, carbene, acyls, methoxycarbonyls, and now alkynes. The further reactivity of this ligand is under exploration in our laboratory, with current efforts directed toward its reaction with olefins and other unsaturated organic substrates.

Experimental Section

The clusters $Ru_3(CO)_{12}$[27] and $Ru_3(\mu_3\text{-NPh})(CO)_{10}$[4a] were prepared according to literature procedures. The reagents PhNO, PhC≡CPh, and $PhC{\equiv}CCH_3$ were purchased from Aldrich Chemical Co. and used as received. Diethyl ether, benzene, THF, and hydrocarbon solvents were distilled from sodium benzophenone ketyl before use, and CH_2Cl_2 was distilled from calcium hydride. Instruments used in this research have been previously described.[28] Elemental analyses were obtained by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Unless otherwise specified, all compound manipulations were done in air.

Reaction of $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ (1) with PhC≡CPh. A solution of 1 (200 mg, 0.30 mmol) and PhC≡CPh (64 mg, 0.36 mmol) in hexane (30 mL) was refluxed under nitrogen for 10 h during which time the yellow solution became burgundy-red. After the solution was cooled to room temperature, the solvent was removed on a rotary evaporator followed by chromatography on silica gel with hexane as eluent. This gave in order of elution a trace of $Ru_3(CO)_{12}$, a yellow band of $Ru_2(CO)_6(\mu_2\text{-}\eta^4\text{-}C_4Ph_4)$ (4,[12] 15 mg, 11%), a yellow band of $Ru_2(CO)_6(\mu_2\text{-}\eta^3\text{-PhC{=}C(Ph)C(O)NPh})$ (2, 84 mg, 65%), and a trace of yellow $Ru_2(CO)_5(\mu_2\text{-}\eta^3\text{-PhC{=}C(Ph)C(O)NPh})\cdot\{Ru_3(\mu_3\text{-NPh})(CO)_6(\mu_3\text{-CO})\}$ (3).

2: IR (hexane) ν_{CO} 2091 (m), 2066 (vs), 2020 (vs), 2002 (s), 1717 (m) cm^{-1}; MS m/z (EI) 669 (M^+); ^1H NMR (CD_2Cl_2) δ 7.26 (br, Ph). Anal. Calcd for $C_{27}H_{15}NO_7Ru_2$: C, 48.43; H, 2.24. Found: C, 48.20; H, 2.45.

3: IR (hexane) ν_{CO} 2085 (s), 2079 (s), 2067 (s), 2060 (s), 2047 (s), 2039 (s), 2026 (vs), 2008 (s), 2002 (m), 1991 (s), 1958 (m), 1850 (w, br), 1736 (w, br), 1692 (w) cm^{-1}; MS, m/z (FD) 1179 ($M^+ - 2CO$).

4: IR (hexane) ν_{CO} 2082 (s), 2043 (vs), 2022 (s), 1998 (vs), 1949 (w) cm^{-1}; MS m/z (EI) 728 (M^+). Anal. Calcd for $C_{34}H_{20}O_6Ru_2$: C, 56.04; H, 2.74. Found: C, 55.89; H, 2.70.

Synthesis of 3 from Reaction of 1 with 2. A solution of 1 (40 mg, 0.060 mmol) and 2 (39 mg, 0.058 mmol) in cyclohexane (30 mL) was refluxed for 48 h under N_2 to give a dark red solution. After the solution was cooled to room temperature, the solvent was removed on a rotary evaporator followed by chromatography on Florisil with hexane/ether (1:1, v/v) as eluent to give 3 (36 mg, 49%) as the second brown band.

Reaction of 1 with PhC≡CMe. A. Thermal Reaction. Complex 1 (400 mg, 0.59 mmol) and PhC≡CMe (92 mg, 0.79 mmol) in cyclohexane (50 mL) were heated at 50 °C for 7 h under N_2 to give a dark orange solution. Column chromatographic separation (SiO_2, hexane/Et_2O eluent with a gradual increase in [Et_2O] from 0% to ~50%) gave a dark yellow band of $Ru_2(CO)_6(\mu_2\text{-}\eta^4\text{-}Ph_2Me_2C_4)$ (7, 12 mg, 4% based on reacted 1) followed by a bright yellow band of a compound tentatively identified as $Ru_4(\mu_4\text{-NPh})(CO)_{11}(MeC{\equiv}CPh)$ (6, 41 mg, 11%), a yellow band of 1 (34.4 mg, 8.6%), a large yellow band of $Ru_2(\mu_2\text{-}\eta^3\text{-PhC{=}CMeC(O)NPh})(CO)_6$ (5, 142 mg, 43%), and a yellow band of $Ru_2(\mu_2\text{-}\eta^3\text{-MeC{=}CPhC(O)NPh})(CO)_6$ (5′, 6 mg, 2%).

5: IR (CH_2Cl_2) ν_{CO} 2093 (m), 2066 (vs), 2020 (vs), 2002 (m), 1686 (m) cm^{-1}; MS m/z (FD) 605 (M^+, ^{101}Ru); ^1H NMR (CD_2Cl_2) δ 7.29 (br, 10 H, Ph), 2.27 (s, 3 H, CH_3). 5′: IR $(CH_2)Cl_2$ ν_{CO} 2093 (m), 2066 (vs), 2018 (vs), 2002 (sh), 1688 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.14 (br, 10 H, Ph), 2.24 (s, 3 H, CH_3); MS m/z (FD) 605 (M^+, ^{101}Ru). Anal. Calcd for $C_{22}H_{13}O_7NRu_2$: C, 43.49; H, 2.14. Found: C, 43.59; H, 2.27.

6: IR (hexane): ν_{CO} 2087 (w), 2060 (s), 2047 (vw), 2033 (vs), 2020 (m), 2012 (m), 1983 (m), 1904 (w), 1854 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.1~6.1 (br, 10 H, Ph), 1.30 (s, 3 H, CH_3); *MS, m/z* (FD) 919 (M^+, ^{101}Ru). Anal. Calcd for $C_{26}H_{13}NO_{11}Ru_4$: C, 33.95; H, 1.14. Found: C, 34.66; H, 1.50.

7: IR (CH_2Cl_2) ν_{CO} 2093 (w), 2076 (sh), 2066 (s), 2039 (vs), 2007 (s) cm^{-1}; MS m/z (EI) 604 (M^+); ^1H NMR (CD_2Cl_2) δ 7.26 (br, 10 H, Ph), 2.24 (s, 0.37 H, CH_3), 2.15 (s, 1.85 H, CH_3), 2.20 (s, 0.78 H, CH_3).

B. Photolysis. A solution of 1 (90 mg, 0.14 mmol) and MeC≡CPh (70 μL, 0.59 mmol) in THF (10 mL) in a sealed quartz vessel under N_2 was irradiated for 12 h with a medium-pressure Hg discharge lamp. The solvent was removed from the resultant brown solution, and the residue was chromatographed as above to give a small yellow band of unreacted 1 (21 mg, 0.031 mmol) followed by a large yellow band of 5 (53 mg, 85%). A third yellow fraction was removed with ether/acetone (1/1), but this species was not further characterized.

C. Using Me_3NO To Eliminate CO. One equivalent of Me_3NO (10.82 mg, 0.15 mmol) in methanol was added dropwise to a solution of 1 (100 mg, 0.15 mmol) in 50 mL of a 1:50 mixture of CH_3CN/THF. The light yellow solution became dark yellow as $Ru_3(\mu\text{-NPh})(CO)_9(CH_3CN)$ formed. Addition of PhC≡CMe (30 mg, 0.17 mmol) caused the solution to immediately turn bright yellow. After the solution was stirred for 80 min at room temperature, the solvent was removed by evaporation. Chromatography of the residue on SiO_2 with hexane/Et_2O eluent gave a yellow band of 5 (29 mg, 32%) followed by two dark yellow bands that were not identified.

Reaction of 2 with PhC≡CPh. A solution of 2 (71 mg, 0.14 mmol) with PhC≡CPh (25 mg, 0.14 mmol) in methylcyclohexane (30 mL) was refluxed for 12 h under N_2 to give a dark red solution.

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Rotary evaporation of solvent followed by TLC separation (SiO_2, hexane/Et_2O = 9/2) gave a yellow band of $Ru_3(CO)_8(\mu\text{-}Ph_4C_4)$ (**10**, 10 mg, 17%) followed by a yellow band of unreacted **2** (31 mg, 0.051 mmol) and a colorless band of pentaphenylpyridinone (**8**, 18 mg, 63%) which was extracted from the SiO_2 with acetone.

8: IR (KBr) ν_{CO} 1640 cm^{-1}; MS *m/z* (EI) calcd for $C_{35}H_{25}NO$ 475.1936, found 475.1919.

10: IR (CH_2Cl_2) ν_{CO} 2070 (m), 2026 (vs), 1975 (s), 1873 (m), 1848 (m)8 cm^{-1}; MS *m/z* (EI) 858 (M^+ - 1CO) plus fragments corresponding to the stepwise loss of six additional CO's.

Reaction of 5 with $PhC\equiv CPh$. A similar reaction to that described above using complex **5** gave formation of tetraphenylmethylpyridinone (**9**) in 53% yield. **9**: IR (CH_2Cl_2) ν_{CO} 1642 cm^{-1}; MS, *m/z* (EI) 413 (M^+).

Reaction of 2 with CO To Form 1,3,4-Triphenylmaleimide. A solution of **2**, (20 mg, 0.030 mmol) in THF (30 mL) was irradiated with a 450-W Hanovia Hg discharge lamp for 12 h under flowing CO in a quartz reaction vessel. Rotary evaporation of solvent followed by chromatographic separation (TLC, SiO_2, hexane/Et_2O, 3:1, v/v) gave only a colorless band of 1,3,4-triphenylmaleimide (**11**, 5.0 mg, 51%). **11**: IR (CH_2Cl_2) ν_{CO} 1723 cm^{-1}; MS *m/z* (EI) 325 (M^+).

X-ray Structural Determinations for Complexes 2, 3, and 5. Crystal, data collection, and refinement parameters are collected in Table I. All crystals were mounted for data collection on glass fibers; initial photographic screening revealed $2/m$ Laue symmetry for all and satisfactory diffraction properties. Data on **3** was limited to $2\theta \leqslant 42°$. Unit-cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections ($20° \leqslant 2\theta \leqslant 24°$) which included Friedel related sets to judge optical and diffractometer alignment. Systematic absences in the diffraction data provided unambiguous space group assignments. Absorption corrections were empirical (ψ-scans, 256 data, six-parameter pseudoellipsoid model).

All structures were solved by direct methods and completed by difference Fourier syntheses. Both **3** and **5** contain two chemically identical enantiomorphs as the crystallographic asymmetric unit. With the exception of the η^6-ring in **3**, all phenyl rings were treated as rigid hexagons (C–C = 1.395 Å). All non-hydrogen atoms were anisotropically refined, and hydrogen atom contributions were idealized (C–H = 0.96 Å).

SHELXTL (5.1) software (Nicolet Corp., Madison, WI) was executed on a Data General Eclipse S-30 computer. Tables of atomic coordinates, structure factors, complete bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates for **2** and **3** are included as supplementary material to ref 8c. Similar data for **5** are given as supplementary material to this paper.

Acknowledgment. We thank the National Science Foundation (CHE8501548) for support of this research and for contributing funds toward the purchase of the X-ray diffractometer at the University of Delaware. Dr. G. Steinmetz and R. J. Hale at the Tennessee Eastman Co. and Dr. R. D. Minard and J. Blank at the Pennsylvania State University are acknowledged for obtaining mass spectra.

Registry No. **1**, 51185-99-0; **2**, 105121-10-6; **3**, 105121-11-7; **4**, 33310-08-6; **5**, 105102-79-2; **5′**, 110294-71-8; **8**, 62557-81-7; **9**, 110271-57-3; **10**, 94658-87-4; **11**, 5191-53-7; $PhC\equiv CPh$, 501-65-5; $PhC\equiv CMe$, 673-32-5.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom positions for **5** (8 pages); a listing of structure factors for **5** (30 pages). Ordering information is given on any current masthead page.

Cinnolinium Salt Synthesis from Cyclopalladated Azobenzene Complexes and Alkynes

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Received March 30, 1987

The reactivity of the cyclopalladated azobenzene chloro dimer is greatly enhanced when the chloro ligands are replaced by tetrafluoroborate ion. The disolvated tetrafluoroborate reacts with a variety of disubstituted alkynes under mild conditions to form 2-phenylcinnolinium tetrafluoroborates in moderate to good yields. The reaction will occur thermally with the cyclopalladated dimer, also, but only in modest yields.

Cinnolinium salts, previously, have been prepared by the alkylation of the corresponding cinnolines. The parent cinnolines were generally obtained by cyclizations of *o*-alkenyl- or similar arenediazonium salts.[1] Frequently, mixtures of 1- and 2-alkylcinnolinium salts were obtained in the alkylation with the 2-isomer predominating. The presence of large substituents at position 3 usually increased the relative amount of 1-alkylation observed.[1] 2-Arylcinnolinium salts, however, were unknown since they could not be obtained by direct arylation.

We have now discovered a convenient route to 2-arylcinnolinium salts in which a variety of substituents may be placed at the 3- and 4-positions.

Results and Discussion

Cyclopalladated azobenzene chloro dimers are readily available from the reaction of azobenzene or its derivatives with palladium chloride at room tempeature.[2-4] These complexes would appear to be convenient starting materials for the preparation of some heterocycles such as cinnolines, but it is known that these complexes are quite stable and generally unreactive[5] except toward carbon monoxide.[6] For example, "phenylpalladium chloride"

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