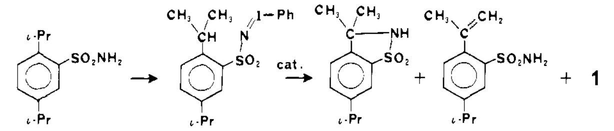
Table I. Catalyzed Reactions of the Imidoiodobenzene Derivative **2** in CH_3CN

	yields[a]		
catalyst	**3**	**4**	**1**
$Fe^{III}(TPP)Cl$	77%	1.4%	12%
$Mn^{III}(TPP)Cl$	16%	4.5%	34%
$[Fe^{III}(cyclam)Cl_2]Cl^b$	42%	4.1%	36%
$FeCl_3$	16%	0.2%	23%
$Rh_2(OAc)_4$	86%	0.2%	5.2%

[a] Yields by HPLC, based on **2**. [b] Cyclam is 1,4,8,11-tetraazacyclotetradecane (ref 10).

showed a ^1H NMR spectrum (in Me_2SO) with methyl doublets at δ 0.92 and 1.21 and methines at δ 2.88 and 3.86, along with a complex aromatic multiplet. The spectrum changed as the sample decomposed. The compound decomposed slowly in air but was stable at −20 °C. It was rapidly reduced by aqueous $NaHSO_3$ to **1** and iodobenzene.

Although **2** was insoluble in most solvents, including CH_3CN and CH_2Cl_2, its reactions could be examined in suspension. In a typical procedure, 44 mg (0.1 mmol) of **2** and 3.5 mg (0.005 mmol) of $Fe^{III}(TPP)Cl$ were stirred in 3 mL of pure degassed CH_3CN. The suspended **2** disappeared in 30 min; after an additional 30 min the solvent was evaporated, and products were analyzed by reverse-phase HPLC. The product mixture consisted of 85% of the insertion product **3** (mp 123.5–124.5 °C),[9] 1.5% of the unsaturated sulfonamide **4**,[9] and 13% of the original sulfonamide **1**. The total yield was 90.4%. Since **2** did not stand up to attempted purification, the missing 10% may partly reflect impure starting material. However, in Table I we list the yield for this and related reactions based on the weight of the starting material **2**; the yields listed are probably underestimates.



1 2 3 4

As Table I shows, $Mn^{III}(TPP)Cl$ was a much inferior catalyst for the insertion reaction and led to a low total yield of the three analyzed products. Similarly, the Fe(III) complex of 1,4,8,11-tetraazacyclotetradecane[10] and $FeCl_3$ itself were inferior to $Fe^{III}(TPP)Cl$. However, $Rh_2(OAc)_4$[11] was an excellent catalyst, forming more insertion product **3** and less of the other products than any other catalyst examined. With the rhodium complex, 94% of the product mixture was **3**.

In the absence of any catalyst the starting material **2** was essentially undecomposed after 1 h suspended in CH_3CN and afforded 65% of **1** and only 1.4% of **3** and 0.3% of **4** after 22 h. However, **2** suspended in carefully purified CH_2Cl_2 decomposed completely in 1 h, affording 26% **3**, 4.5% **4**, and 24% **1**. The reactions with $Fe^{III}(TPP)Cl$ or $Mn^{III}(TPP)Cl$ were poorer in CH_2Cl_2, only 35% of the insertion product **3** forming with the $Fe^{III}(TPP)Cl$ catalyst. CH_2Cl_2 has often been used as solvent in other P-450 model systems.[2-6] Poor yields of insertion product **3** were also obtained on thermolysis of **2** or thermolysis or photolysis of the corresponding sulfonyl azide.[12] Strikingly, our intramolecular insertion process is much better with an iron porphyrin than a manganese porphyrin catalyst, in contrast to previous model systems[1,2-5] but in analogy to the natural enzymatic system. Furthermore, in both CH_3CN and CH_2Cl_2 the manganese catalyst afforded proportionately more olefin product **4** compared with insertion product **3**. Thus the optimum for a clean reaction uses the imidoiodobenzene derivative **2** in CH_3CN with $Fe^{III}(TPP)Cl$ or $Rh_2(OAc)_4$ as catalysts.

As expected, converting our original intermolecular tosylamidation of cyclohexane with $Fe^{III}(TPP)Cl$ or $Mn^{III}(TPP)Cl$ catalysis[1] to an intramolecular directed metal–nitrene insertion reaction has greately improved its efficiency. It remains to be seen whether our reaction can be generalized to a "remote functionalization" reaction,[13] involving intramolecular or intracomplex reactions over larger distances. If so, this analogue of an enzymatic hydroxylation could prove to be a very useful synthetic reaction.

Acknowledgment. Support by the National Science Foundation and by an NIH training grant are gratefully acknowledged.

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(9) Characterized by NMR and mass spectroscopy.

(10) Chan, P.-K.; Poon, C.-K. *J. Chem. Soc., Dalton trans.* **1976**, 858.

(11) $Rh_2(OAc)_4$ has been used to elicit carbene reactivity from diazo compounds; for an example, see: Taber, D. F.; Petty, E. H. *J. Org. Chem.* **1982**, *47*, 4808. A. W. Schwabacher (unpublished work) has used it with phosphoryl azides to catalyze nitrene insertions.

(12) 2,5-Diisopropylbenzenesulfonyl azide was also inert to $Rh_2(OAc)_4$, $Fe^{III}(TPP)Cl$, and $Mn^{III}(TPP)Cl$ in refluxing acetonitrile.

(13) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.

Why Terminal Alkynes Cannot Be Metathesized. Preparation and Crystal Structure of a Deprotonated Tungstenacyclobutadiene Complex, $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2]Cl$[1a]

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During our ongoing studies aimed at determining the scope of metathesis of alkynes[2] by $W(CR)(OCMe_3)_3$,[3] we found that terminal alkynes could not be metathesized. We believe we now know why.

$W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl_2$,[4] a molecule that will *not* metathesize alkynes, reacts with $Me_3CC{\equiv}CH$ in ether to give approximately equal amounts of two products in high yield. One is red, soluble in pentane, and analyzes as $WCp[C_3(CMe_3)_2]Cl$ (**1**, Cp = $\eta^2\text{-}C_5H_5$);[5a] the other is orange, soluble in dichloromethane (not pentane), and analyzes as $WCp[C_3H_2(CMe_3)_2]Cl_3$ (**2**).[5b] Addition of 2 equiv of HCl to **1** gives **2** essentially quantitatively. If triethylamine is present in the reaction between $WCp(CCMe_3)Cl_2$ and *tert*-butylacetylene only the red product is produced along with 1 equiv of NEt_3HCl (eq 1). We have not been able to convert **2** to **1** with triethylamine or $Ph_3P{=}CH_2$.

$$WCp(CCMe_3)Cl_2 + Me_3CC{\equiv}CH \xrightarrow{Et_3N} WCp[C_3(CMe_3)_2]Cl + NEt_3HCl \quad (1)$$

NMR and IR data suggest that **2** is a *tert*-butyl (*tert*-butylvinyl-substituted)methylene complex, i.e., $CpCl_3W{=}C(CMe_3)[trans\text{-}HC{=}CH(CMe_3)]$.[6] This proposal is strengthened

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(1) (a) Multiple Metal–Carbon Bonds. 34. (b) Massachusetts Institute of Technology. (c) State University of New York at Buffalo.

(2) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (b) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75.

(3) (a) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291. (b) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645.

(4) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046.

(5) (a) Anal. Calcd for $WC_{16}H_{23}Cl$: C, 44.21; H, 5.33; Cl, 8.16. Found: C, 44.56; H, 5.51; Cl, 8.10. (b) Anal. Calcd for $WC_{16}H_{25}Cl_3$: C, 37.86; H, 4.96; Cl, 20.95. Found: C, 38.23; H, 5.03; Cl, 20.88.

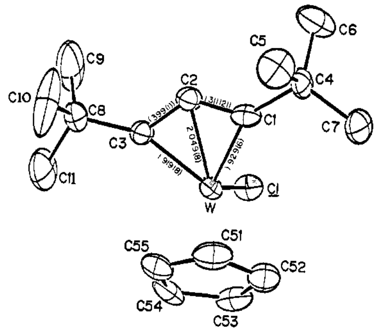


Figure 1. The $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2]Cl$ molecule, projected onto its WC_3 plane and showing bond lengths of interest. (Hydrogen atoms of the $\eta^5\text{-}C_5H_5$ and $C_3(CMe_3)_2$ ligands are omitted for the sake of clarity.)

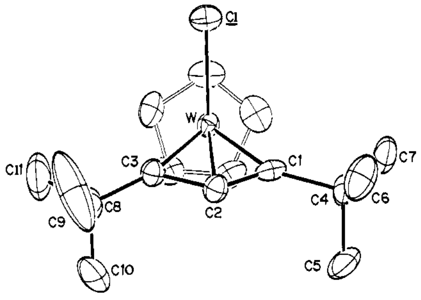
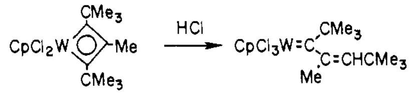


Figure 2. The $W(\eta^2\text{-}C_5H_5)[C_3(CMe_3)_2]Cl$ molecule, projected onto the plane of the $\eta^5\text{-}C_5H_5$ ligand. Note the approximate C_s (m) symmetry.

by the fact that $WCpCl_2[C_3(CMe_3)_2Me]$[7] reacts with 1 equiv of HCl in ether to give an analogous complex[8] (eq 2; configuration about the C═C bond is unknown).



(2)

The nature of **1** was considerably more difficult to deduce. On the basis of its ^{13}C NMR spectrum,[9] we suspected that it might be a cyclopropenylidene complex, the first type of carbene complex to be discovered that did not contain a stabilizing heteroatom.[10] However, two facts militated against such a formulation. First, **1** would almost certainly be dimeric and therefore not so soluble in pentane. Second, even if it were dimeric we could not rationalize the fact that it does not react readily with CO, 3-hexyne, *cis*-2-pentene, ethylene, oxygen, water, $LiOCMe_3$, LiMe, MeI, or $Me_3O^+BF_4^-$. An X-ray structure[11] revealed that **1** is actually the dehydrohalogenated version of its likely tungstenacyclobutadiene precursor, $WCpCl_2[C_3H(CMe_3)_2]$ (cf. $WCpCl_2[C_3Ph_2(CMe_3)]$[4]).

The molecular geometry of $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2]Cl$ is illustrated in Figures 1 and 2. The W–C(1)–C(2)–C(3)–C(4)–C(8) system is planar within the limits of experimental error and all three W–C(x) (x = 1, 2, 3) bond distances are relatively short. (Internal angles are C(3)–W–C(1) = 79.4 (5)°, W–C(1)–C(2) = 75.8 (7)°, C(1)–C(2)–C(3) = 130.2 (9)°, and C(2)–C(3)–W = 74.5 (5)°.) Within the $C_3(CMe_3)_2$ ligand the 0.088-Å difference in the carbon–carbon distances of C(1)–C(2) = 1.311 (21) Å and C(2)–C(3) = 1.399 (11) Å is, unfortunately, on the borderline of statistical significance because C(2) is common to the two measurements. Needless to say, the lack of reactivity of this complex is all the more remarkable considering the extraordinary environment of C(2). The short W–C(β) distance and substantial $J_{C(\beta)W}$ (26 Hz;[9] not observed in $WCpCl_2(C_3R_3)$ complexes[4]) suggest that the two electrons previously in the CβH bond are now in essentially a W–C(β) σ type bonding orbital.[14]

In comparison with the planar W[C(CMe$_3$)C(Me)C(Me)] system in W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$,[15] the "deprotonated" W[C$_3$(CMe$_3$)$_2$] complex differs in the following ways: (i) the W–C(α) distances are slightly longer (1.929 (6) and 1.919 (8) Å vs. 1.861 (9) and 1.864 (8) Å); (ii) the W–C(β) distance is significantly shorter (2.049 (8) Å vs. 2.115 (8) Å); (iii) the C(α)–C(β)–C(α') angle is larger (130.2 (9)° vs. 118.9 (8)°); (iv) the C(α)–C(β) and C(α')–C(β) distances are shorter (1.355 Å (average) as compared to 1.467 Å (average)).

Evidence that "deprotonated" tungstenacyclobutadiene complexes can be formed in *active* alkyne metathesis systems is shown in eq 3. The ^{13}C NMR spectrum[16] of red, crystalline W-

$$W(CPh)(OCMe_3)_3{}^{2a} + PhC{\equiv}CH \xrightarrow[-Me_3COH]{+2(py)} W(OCMe_3)_2(C_3Ph_2)(py)_2 \quad (3)$$

$(OCMe_3)_2(C_3Ph_2)(py)_2$ is so similar to that of **1** that we feel it too must be a deprotonated metallacycle formed by loss of *tert*-butyl alcohol from incipient $W(OCMe_3)_3(C_3HPh_2)$. In particular, the peak located at 174 ppm assignable to C(β), although it is broader than that at 197 ppm for C(β) in $WCp[C_3(CMe_3)_2]Cl$, shows barely resolvable tungsten satellites, suggesting that $J_{C(\beta)W}$ in this case is also substantial (estimated 20–30 Hz).

Although the proof is not yet complete, we feel that the evidence available at this juncture that we have presented here suggests strongly that a proton can be lost readily from a carbon atom in a tungstenacyclobutadiene complex and that this is the reason why terminal alkynes have not yet been metathesized successfully. We think they are likely to be only if masked as trimethylsilyl derivatives.

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Supplementary Material Available: Listing of final positional and thermal parameters and a list of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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[6] ^1H NMR (C_6D_6) δ 8.38 (d, 1, $^3J_{HH}$ = 15.4, olefinic H), 7.14 (d, 1, $^3J_{HH}$ = 15.4, olefinic H), 5.72 (s, 5, C_5H_5), 1.20 (s, 9, CMe$_3$), 1.02 (s, 9, CMe$_3$); ^{13}C NMR (CD_2Cl_2) δ 301.8 (s, J_{CW} = 74, C(α)), 187.3 (d, J_{CH} = 162, olefinic C), 107.9 (d, J_{CH} = 188, Cp), 104.4 (d, J_{CH} = 164, olefinic C), 53.7 (*C*Me$_3$), 38.6 (*C*Me$_3$), 31.2 (q, J = 127, C*Me*$_3$), 27.0 (q, J_{CH} = 127, C*Me*$_3$); IR (Nujol) 1570 cm^{-1}.

[7] This compound was prepared as reported previously.[4] Anal. Calcd for $WC_{17}H_{26}Cl_2$: C, 42.09; H, 5.40. Found: C, 41.75; H, 5.46.

[8] Partial ^{13}C NMR (CD_2Cl_2) δ 304.5 (s, J_{CW} = 67, C(α)), 160.5 (d, J_{CH} = 160, C_{ol}), 117.4 (s, C_{ol}).

[9] ^{13}C NMR (C_6D_6) δ 220.4 (s, J_{CW} = 127), 197.1 (s, J_{CW} = 26), 98.1 (d, J_{CH} = 179, Cp), 44.4 (*C*Me$_3$), 32.1 (q, J_{CH} = 126, C*Me*$_3$).

[10] Öfele, K. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 950.

[11] The complex crystallizes in the noncentrosymmetric orthorhombic space group $Pna2_1$ [C^9_{2v}; No. 33] with a = 12.681 (1) Å, b = 15.373 (3) Å, c = 8.777 (1) Å, V = 1711 (1) Å^3, and ρ(calcd) = 1.69 g cm^{-3} for Z = 4 and M_r 434.69. Diffraction data for the two octants hkl and hk$\bar{l}$ were collected on a Syntex P2$_1$ automated four-circle diffractometer via a coupled θ(crystal)–2θ(counter) scan technique[12] and were corrected for Lorentz and polarization factors and the effects of absorption (μ(Mo Kα) = 72.8 cm^{-1}). The structure was solved by a combination of Patterson, difference-Fourier, and least-squares refinement techniques. All non-hydrogen atoms were located directly and refined using anisotropic thermal parameters; hydrogen atoms of the C_5H_5 and $C_3(CMe_3)_2$ ligands were included in calculated positions with d(C–H) = 0.95 Å and the appropriate idealized planar (C(sp^2)–*H*) or staggered tetrahedral (C(sp^3)–*H*) positions.[13] Convergence was reached with R_F = 4.2% and R_{wF} = 3.1% for 162 parameters refined against 3021 point-group independent reflections with 2θ = 4.5–50.0° (Mo Kα); R_F = 3.1% and R_{wF} = 2.9% for those 2638 data with $|F_o| > 3\sigma(|F_o|)$. These values all correspond to refinement with the correctly defined crystal chirality. The molecular geometry has a tendency toward noncrystallographic C_s (m) symmetry (cf. Figure 2), but this does not coincide with the possibility of a mirror plane at $z = {}^1/_4$ which could convert the space group to the centrosymmetric *Pnam*.

[12] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

[13] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[14] A referee suggested viewing the R_2C_3 fragment as a derivative of a linear R–C–C–C–R unit containing two orthogonal π-systems, one being used to form "three σ bonds" to W and the other to form the extended π-system.

[15] Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1983**, *104*, 6808.

[16] ^{13}C NMR ($CDCl_3$) 189.5 (s, $J_{CW} \approx$ 130, *C*(Ph)C*C*(Ph)), 173.9 (s, J_{CW} = 20–30, C(Ph)*C*C(Ph)), 150.1 (d, J_{CH} = 174, ortho C), 141.8 (s, ipso C), 136.8 (d, J_{CH} = 159, meta C), 131.5 (d, J_{CH} = 159, ortho C), 128.1 (d, J_{CH} = 157, meta C), 125.4 (d, J_{CH} = 133, para C), 123.8 (d, J_{CH} = 167, para C), 78.0 (s, O*C*Me$_3$), 31.9 (q. J_{CH} = 126, OC*Me*$_3$).