Controlled, Reversible Conversion of a Ketene Ligand to Carbene and CO Ligands on a Single Metal Center

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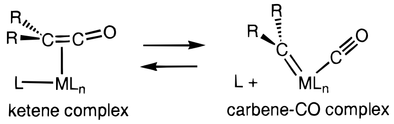
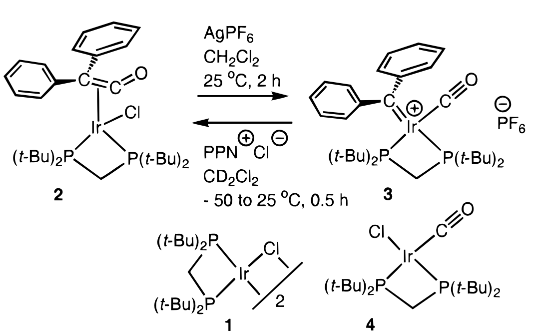
The formation of ketenes from metal-coordinated carbenes and CO is implicated as a key step in several useful synthetic reactions. Carbene−CO complexes (eq 1) can be used as sources of ketene intermediates in benzannulation reactions,[1] ketene−imine or ketene−alkene cycloadditions,[2] or electrophilic substitution reactions.[3] In a few cases, ketene ligands have actually been observed on single metal centers after coupling of carbene and CO ligands.[4−6] In contrast, the reverse reaction, cleavage of a ketene ligand to carbene and CO ligands, has never been seen on a single metal center, until this work. The interaction of ketenes with some transition metal complexes has given carbene complexes, but these reactions have led to *dinuclear*[7,8] *or trinuclear*[9] carbene complexes featuring a bridging carbene ligand, which is not related to ketene-forming reactions used in organic synthesis. Among *mono*nuclear systems, a few ketene complexes have been shown to decompose to metal−CO complexes and alkenes (probable carbene dimerization products).[10,11] Starting with an iron−ketene complex, incorporation of external ^{13}CO into the bound ketene ligand has been seen, presumably by way of an undetected carbene−CO intermediate.[12] However, from these reactions a carbene−CO complex has not yet been isolated. Here, we report such an occurrence for the first time. Removal of a chloride ligand from a 16-electron Ir−ketene complex breaks the ketene C═C bond, giving an Ir complex with carbene and CO ligands, characterized by X-ray diffraction. Moreover, the carbene and CO ligands can be recoupled upon addition of chloride. This opens the way to studying the fundamental interconversion illustrated by eq 1 in both directions on the same metal fragment ML$_n$.



(1)

Our strategy for studying ketene cleavage was to prepare a ketene complex with a ligand which could be easily removed under mild conditions. We hoped that removal of such a ligand *cis* to the ketene would lower the formal electron count and result in breaking the ketene ligand into carbene and CO ligands *cis* to each other. Our experience with ketene complexes of *trans*-ClM(PR$_3$)$_2$ (M = Ir[13−15] or Rh[16]) fragments has thus far involved monodentate, bulky phosphines PR$_3$, in which two phosphines appear mutually *trans* to each other, leaving the two remaining coordination sites *trans*, not *cis* as desired. Therefore, the use of a chelating diphosphine was explored. Combination of the phosphine (t-Bu)$_2$PCH$_2$P(t-Bu)$_2$ (dtbpm) with the iridium(I) dimer [(μ-Cl)Ir(cyclooctene)]$_2$ leads to a very air-sensitive cyclooctene-free species, formulated as halide-bridged dimer **1**.[17] When this ligand exchange reaction is performed in the presence of diphenylketene, ketene complex **2** is formed in 61% yield. The η^2-(*C*,*C*) binding of the ketene ligand in **2** was suggested by the strong IR absorption at 1728 cm^{-1} and the ^{13}C NMR shifts of the ketene carbons [195.50 (dd, J = 6.2, 3.5 Hz, O═*C*═C) and 23.6 (d, J = 47.5 Hz, O═C═*C*)].[13,16,18] Furthermore, the fact that all four ortho protons appeared as a single resonance was consistent with an η^2-(*C*,*C*) complex, whereas an η^2-(*C*,*O*) isomer (not shown) would have inequivalent phenyl groups. We note that the same phosphine and same ketene on Ni(0) gave an η^2-(*C*,*O*) complex.[19] The phosphorus nuclei in **2** are inequivalent (−8.39 and −22.39 ppm, two doublets, J = 30.3 Hz). An X-ray diffraction study verified the proposed structure (Figure 1),[20] only the fifth structure of a ketene in η^2-(*C*,*C*) binding mode.[21−24] Complex **2** cannot be described as having square planar geometry.



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(1) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587−608.

(2) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105−4128.

(3) Bueno, A. B.; Moser, W. H.; Hegedus, L. S. *J. Org. Chem.* **1998**, *63*, 1462−1466.

(4) Herrmann, W. A.; Planck, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525−526.

(5) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926−5928.

(6) Schwab, P.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1480−1482.

(7) Hong, P.; Nishii, N.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1972**, 993.

(8) Yamamoto, T.; Garber, A. R.; Wilkinson, J. R.; Boss, C. B.; Streib, W. E.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* **1974**, 354−356.

(9) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 364−365. See also Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783−4789.

(10) Miyashita, A.; Shitara, H.; Nohira, H. *Organometallics* **1985**, *4*, 1463−1464.

(11) Miyashita, A.; Sugai, R.; Yamamoto, J. *J. Organomet. Chem.* **1992**, *428*, 239−247. η^2-(*C*,*O*)−(CH$_2$═C═O)Ni(PCy$_3$)$_2$ is known: Wright, C. A.; Thorn, M.; McGill, J. W.; Sutterer, A.; Hinze, S. M.; Prince, R. B.; Gong, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 10305−10306.

(12) Bkouche-Waksman, I.; Ricci, J., J. S.; Koetzle, T. F.; Weichmann, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492−1499.

(13) Grotjahn, D. B.; Lo, H. C. *Organometallics* **1995**, *14*, 5463−5465.

(14) Grotjahn, D. B.; Lo, H. C. *J. Am. Chem. Soc.* **1996**, *118*, 2097−2098.

(15) Lo, H. C.; Grotjahn, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 2958−2959.

(16) Grotjahn, D. B.; Bikzhanova, G. A.; Hubbard, J. L. *Organometallics* **1999**, *18*, 5614−5619.

(17) (a) Meier, C. Diplomarbeit, Technische Universität München, 1989. An X-ray crystal structure[17b] and thorough study of the chemistry of the dimer [ClRh(dtbpm)]$_2$ and the fragment ClRh(dtbpm)[17c] have been reported by Hofmann's group. (b) Hofmann, P.; Meier, C.; Hiller, W.; Heckel, M.; Riede, J.; Schmidt, M. U. *J. Organomet. Chem.* **1995**, *490*, 51−70. (c) Hofmann, P.; Meier, C.; Englert, U.; Schmidt, M. U. *Chem. Ber.* **1992**, *125*, 353−365.

(18) Geoffroy, G. L.; Bassler, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1−83.

(19) Hofmann, P.; Perez-Moya, L. A.; Steigelmann, O.; Riede, J. *Organometallics* **1992**, *11*, 1167−1176.

(20) Orthorhombic, *Pbca*, orange plate, 0.40 mm × 0.20 mm × 0.10 mm, a = 11.5550(2) Å, b = 20.3396(2) Å, c = 27.4672(2) Å, V = 6455.45(11) Å^3, Z = 8, T = 173 K, D_{calc} = 1.495 g cm^{-3}, R1 = 3.09%, wR2 = 11.26% for 7270 observed independent reflections, GOF = 1.014.

(21) Redhouse, A. D.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 615−616.

(22) Herrmann, W. A.; Plank, J.; Ziegler, M.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133−3135.

(23) Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* **1984**, *264*, 327−352.

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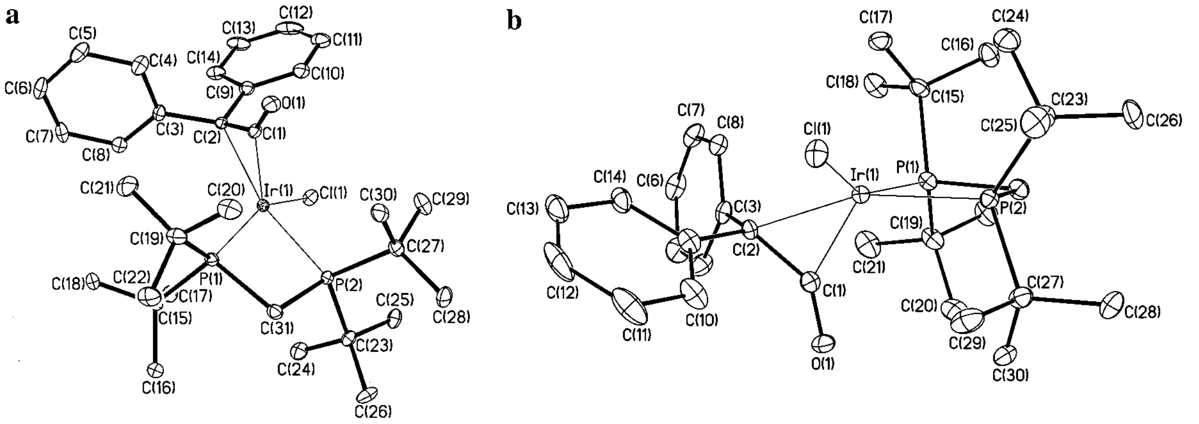

Figure 1. ORTEP diagrams of **2**. Thermal ellipsoids at 30% probability. Hydrogens have been omitted for clarity. Key bond distances (Å) and angles: C(1)−C(2), 1.488(7); C(1)−O(1), 1.222(6); Ir−C(1), 1.986(5); Ir−C(2), 2.245(4); Ir−P(1), 2.3176(12); Ir−P(2), 2.3833(11); Ir−Cl(1), 2.3941(12); P(1)−Ir−P(2), 73.59(4); P(1)−Ir−Cl(1), 152.16(4); P(2)−Ir−Cl(1), 91.78(4). Figure 1b emphasizes the distortion from square planar geometry. Distances of coordinated atoms from to the plane defined by P(1), Ir, and P(2): center of the C(1)−C(2) bond, 1.206(5) Å; C(1), 1.694(5) Å; C(2), 0.716(5) Å; Cl(1), −0.976(2) Å (+ and − values signify points on opposite sides of the plane).

The narrow P(1)−Ir−P(2) angle [73.59(4)°] enforced by the one-carbon bridge of the diphosphine ligand is to be expected.[17b,25] However, the profound deviation from square-planar geometry is shown by Figure 1b. The ketene C═C bond [as defined by the C(1)−C(2)−O(1) plane] is almost orthogonal (82.9°) to the P−Ir−P plane. In **2**, the C−C bond of the ketene is the longest reported among η^2-(*C*,*C*)-bound ketenes.[21−24]

When an orange solution of **2** in CD_2Cl_2 or CH_2Cl_2 is treated with 1 equiv of $AgPF_6$ to remove the chloride ligand, darkening of the solution color begins immediately. Spectral data indicate that within 2 h, formation of the deep red-brown complex **3** is complete. Filtration and use of benzene allows crystallization of **3** in 53% yield. A pure sample of **3** in solution is stable at room temperature for several days. The ligand set in **3** is clear from the spectral data. A CO ligand in **3** is indicated by IR (ν_{CO} 1999 cm^{-1}, very strong absorption) and ^{13}C NMR [181.63 ppm (d, J = 78.6 Hz)] data. Most importantly, the presence of a carbene ligand is secured by observation of a signal far downfield at 326.1 ppm (dd, J = 2.0, 60.9 Hz). The effect of a deshielding carbene ligand on the ipso carbons of the phenyl rings is shown by their downfield chemical shift (δ 158.87 ppm), compared to 144.31 ppm for the same carbons in **2**.[26] In distinct contrast to what is seen in **2**, the crystal structure of **3** (Figure 2)[27] reveals a somewhat distorted square-planar geometry: the central Ir and four atoms directly bound to it are within 0.084 Å of the plane defined by those five atoms. The $Ir{=}CPh_2$ distance of 1.996(8) Å can be compared to a shorter M═C distance of 1.868(9) Å in an Ir(I)═CH_2 complex[28] and a similar distance of 1.997(5) Å in an Ir(I)−dialkylcarbene complex,[29] and to the $M{=}CPh_2$ distances of 1.863(4) Å in *trans*-$(Cl)Rh(CPh_2)[Sb(i\text{-}Pr)_3]_2$,[6] and 2.13−2.15(2) Å in $(CO)_5W(CPh_2)$.[30] The large diphenylcarbene ligand experiences more steric repulsion with the nearby P(*t*-Bu)$_2$ groups than does the CO ligand [angle P(1)−Ir−C(1) = 101.1(2)°, angle P(2)−Ir−C(14) = 93.9(3)°].

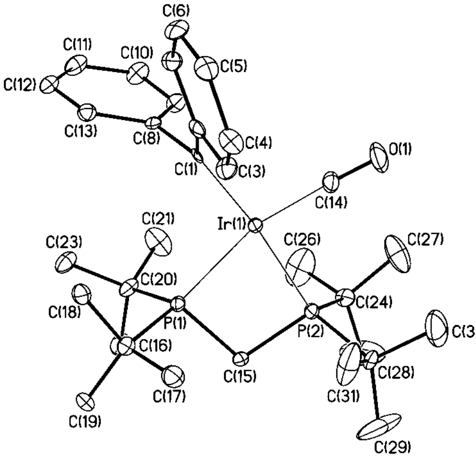

Figure 2. ORTEP diagram of **3**. Thermal ellipsoids at 30% probability. Hydrogens and PF_6^- ion have been omitted for clarity. Key bond distances (Å) and angles (deg): Ir−C(1), 1.996(8); Ir−C(14), 1.859(9); C(14)−O(1), 1.133(11); Ir−P(1), 2.417(2); Ir−P(2), 2.391(2); P(1)−Ir−P(2), 72.92(7); P(1)−Ir−C(1), 101.1(2); P(2)−Ir−C(14), 93.9(3); C(1)−Ir−C(14), 91.8(3).

Significantly, reaction of **3** with chloride ion regenerates **2**, with the intact ketene ligand. Addition of a solution of the salt $[Ph_3P{=}N{=}PPh_3]Cl$ in CD_2Cl_2 to a deep red solution of **3** in CD_2Cl_2 at room temperature led to loss of the carbene ligand, but when the addition was performed at −50 °C, with subsequent warming to room temperature within 0.5 h, a brownish-orange solution containing both ketene complex **2** (64%) and CO complex **4** (31%) was formed. Conditions for the regeneration of **2** from **3** have not yet been optimized, but *the results clearly show that we have found a system for studying both ketene cleavage and formation on a single metal center for the first time.* The extension of our strategy to other ketenes and metal fragments, so as to study the influence of steric and electronic factors on the fundamental interconversion identified in eq 1 is under active investigation in our laboratory, and will be reported in due course.

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Supporting Information Available: Complete details of the X-ray diffraction study on **2** and **3** and NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Bleuel, E.; Laubender, M.; Weberndörfer, B.; Werner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 156−159.

(25) Hofmann, P.; Meier, C.; Englert, U.; Schmidt, M. U. *Chem. Ber.* **1992**, *125*, 353−365.

(26) The resonances described so far are sharp in spectra obtained at 30 °C, but the proton resonances for the *t*-Bu groups and the phosphorus nuclei are broadened unless spectra are obtained at − 20 to 0 °C.

(27) Monoclinic, $P2_1/c$, brown block, 0.25 mm × 0.20 mm × 0.10 mm, a = 9.3207(5) Å, b = 28.2934(17) Å, c = 12.8302(7) Å, β = 98.579(2)°, V = 3345.6(6) $Å^3$, Z = 4, T = 173 K, D_{calc} = 1.659 g cm^{-3}, R1 = 4.37%, wR2 = 9.80% for 4920 observed independent reflections, GOF = 1.086.

(28) Fryzuk, M. D.; MacNeil, P.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708−6710.

(29) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217−1224.

(30) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127−2134.