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Reactivity of η^2-(C,O)-Bound Ir−Ketene Complexes: A 1,3-Hydride Shift Is a Hydride Walk by Way of an Enol Complex

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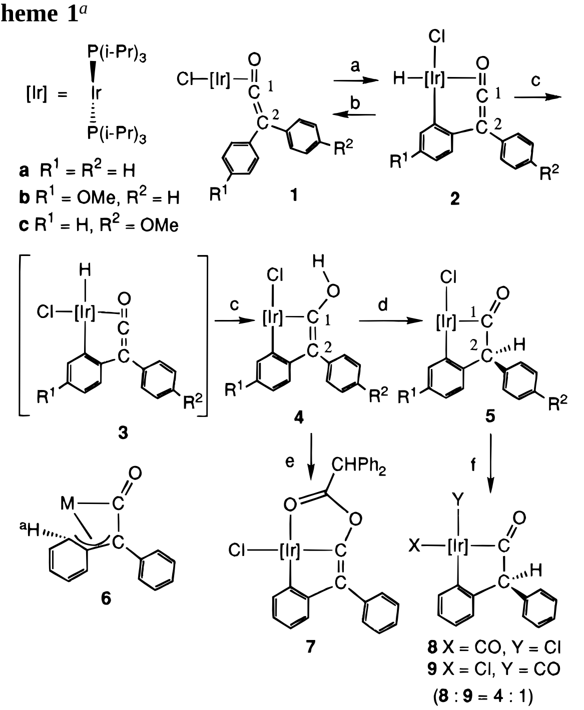
Metal−ketene complexes[1] have been suggested as intermediates in reductions of CO and CO_2 in industrially important processes.[2] Ketene complexes have been implicated as crucial intermediates in thermal reactions (e.g., the Dötz reaction)[3] and in photoinduced transformations of Fischer carbene complexes, although in the latter case such species have yet to be detected spectroscopically or isolated.[4] Side products in both thermal and photochemical reactions of Fischer carbene complexes suggest that intramolecular C−H bond activation of either carbene or ketene intermediates is possible,[5] but this has not been demonstrated on an isolable ketene complex.[1] Here we report that structurally characterized Ir−ketene complexes **1**[6] undergo C−H bond activation both thermally and photochemically. Quantitative photochemical conversion of **1** at −25 °C to a *cis*-aryl(hydride)Ir(III) complex **2** is cleanly reversed at ambient temperature. A net 1,3-hydride shift (**1** → five-coordinate acyl **5**) is shown to be the result of a four-step *hydride walk*, by way of **2**, **3**, and **4** (Scheme 1). The last intermediate (**4**) is a five-coordinate enol complex which, like its acyl tautomer **5**, adds CO stereoselectively.

Complex **1a**[6] could be produced by direct complexation to $Ph_2C{=}C{=}O$[7] (88% after chromatography over SiO_2). Heating a solution of **1a** in C_6D_6 (80−90 °C, 8−9 h) led to **5a** in 88−92% yield. The ^1H NMR spectrum of **5a**[8] showed resonances for nine aromatic protons, a one-proton singlet at δ 4.52, and absorptions for two $P(i\text{-}Pr)_3$ ligands. In the $^{31}P\{^1H\}$ NMR spectrum, an AB pattern with large coupling (313.3 Hz) indicated inequivalent, mutually trans phosphines. In the ^{13}C spectrum (C_6D_6), only two triplets were seen, at δ 195.92 (J = 3.2 Hz) and 139.03 (J = 7.0 Hz), supporting the assignment of an acyl carbon and an aryl carbon bound to the $IrCl[P(i\text{-}Pr)_3]_2$ unit. Save for the lack of observable coupling to the proton resonating at δ 4.52 ppm, these data might be consistent with formulation of the new product as **6** {M = $IrCl[P(i\text{-}Pr)_3]_2$},[9a] but NOE information[8,9b] and the facile addition of CO discussed below confirm structure **5a**. In contrast to **6**, **5a** is derived (formally) from **1a** by ortho-metalation and a 1,3-hydride shift.

Scheme 1[a]



[a] (a) Pyrex-filtered UV light, toluene-d_8, −25 °C, ≤10 min, 100%; (b) room temperature, ≤10 min, 100%; (c) same as (a) but in C_6D_6 at 28−30 °C, 10 h, 78% of **4a** from **1a**; (d) C_6D_6, room temperature, 1 day, 100%; (e) for **4a**, $Ph_2C{=}C{=}O$, C_6D_6, room temperature, 1 h, 97% (75% from **1a**); (f) for **5a**, CO, 1 atm, room temperature, 2 min.

How has this hydride shift occurred? In the thermolysis reaction just described, intermediates were not detected in NMR spectra of the mixture. However, irradiating a solution of **1a** in toluene-d_8 with Pyrex-filtered UV light at −25 °C for only 10 min produced **2a** in quantitative yield based on integration against an internal standard. In the ^1H NMR spectrum of **2a**,[8] an upfield triplet (δ −11.21, J_{PH} = 10.5 Hz) and resonances in the region 6.5−7.9 ppm for nine protons pointed to oxidative addition of an ortho-CH bond to the metal. One singlet in the $^{31}P\{^1H\}$ NMR spectrum[10] implicated the symmetry of an η^2-(C,O)-bound ketene complex, and ^{13}C NMR and IR data were consistent with reduced back-bonding in **2a** compared with that in **1a**.[11] Remarkably, on standing at ambient temperature for 10 min, **2a** reverted to **1a** quantitatively. Furthermore, geometric isomers **1b**,**c** stereospecifically furnished the corresponding thermally unstable products **2b**,**c**.[8] Thus, the behavior of **1** and **2** is a rare example of a photochromic organometallic reaction.[12]

Although **2a** reverted to **1a** in a dark reaction, prolonged irradiation of **1a** at higher temperatures (28−30 °C, 10 h) gave

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(1) (a) Geoffroy, G. L.; Bassler, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1−83. (b) For an especially good leading reference, see: Hofmann, P.; Perez-Moya, L. A.; Steigelmann, O.; Riede, J. *Organometallics* **1992**, *11*, 1167−1176 and references therein. (c) Review of recent ketene chemistry: Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273−279.

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

(7) $Ph_2C{=}C{=}O$ and $P(i\text{-}Pr)_3$ were added to $[(\mu\text{-}Cl)Ir(cyclooctene)_2]_2$ in C_6D_6 at 25 °C (molar ratio 1.0:2.0:0.5), and **1a** was isolated after 0.5 h.

(8) ^1H, ^{13}C, and ^{31}P NMR and IR data for all new compounds are available as supporting information. Thermally stable compounds were further characterized by elemental analysis.

(9) (a) The compound **6** [M = $Fe(CO)_3$] was formed (38%) by reaction of $Ph_2C{=}C{=}O$ with $Fe(CO)_5$, and its ^1H NMR spectrum exhibited a narrow doublet (J = 5.6 Hz) at 4.42 ppm for ^aH: Bkouche-Waksman, I.; Ricci, J. S., Jr.; Koetzle, T. F.; Weichmann, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492−1499 and references to earlier work. (b) Key NOE data[8] for **5a** which discounted **6**: 90% saturation of the singlet at δ 4.52 led to strong enhancement (7.0%) of the two-proton doublet for the ortho protons of the C_6H_5 ring, as well as 1.8% enhancement of the one-proton doublet for the nearest proton on the metalated ring.

(10) A complex of $ClIr[P(i\text{-}Pr)_3]_2$ with a (C,C)-bound ketene bearing different substituents on the terminal carbon would be expected to show two ^{31}P resonances. See also ref 6.

(11) For **2a**: ^1H NMR (toluene-d_8, −27 °C) δ 192.93 (t, J_{PH} = 1.9 Hz, C1), 85.63 (s, C2); IR (toluene-d_8, NaCl) 2336 (Ir−H), 1742, 1464. For **1a**: ^1H NMR (C_6D_6, ambient) δ 143.39 (t, J_{PH} = 3.2 Hz, C1), 74.26 (s, C2); IR (KBr) 1636, 1589 cm^{-1}.

(12) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790−2795. Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676−1677.

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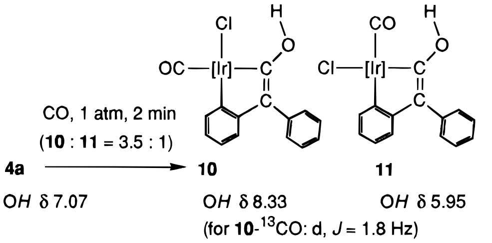
rise to a mixture containing products **5a** (6%), the known *trans*-(CO)IrCl[P(*i*-Pr)$_3$]$_2$ (11%),[13,14] and **4a** (78%, versus internal standard). The new complex **4a** bears equivalent ^{31}P nuclei, and its ^{1}H NMR spectrum showed resonances for nine aromatic protons as in **2a** or **5a**, but in addition, a sharp one-proton singlet at 7.07 ppm, which disappeared on shaking with D_2O.[15a] Moreover, **4a** exhibited a weak, broad IR absorption near 3350 cm^{-1}, as seen in spectra of organic enols,[15b] and this shifted to 2470 cm^{-1} on exchange with D_2O. ^{13}C NMR and HMBC data for **4a** indicated that the resonances for the HOC=C unit appeared at δ 150.07 (t, $J = 6.5$ Hz, C1) and 127.29 (t, $J \approx 1$ Hz, C2). The spectral evidence in favor of an enol formulation was corroborated by tautomerization of **4a** to **5a** on standing in solution in the dark (half-life ca. 15 h) or on attempted chromatography over silica gel. Similarly, **4a**-*O-d* isomerized to **5a**-*C2-d* over 1 day. Control experiments were undertaken to characterize the prototropy in **4a** and **5a**. In the dark, **5a** showed no evidence[16] of deuteration at C2 after 2 days with D_2O at 30 °C, or after 8 h at 80 °C. Addition of DCl (0.25 equiv) to the mixture resulted in 60% deuteration of **5a** at C2 after 2 h at 80 °C (with some decomposition). Irradiation of **5a** did not lead to **4a**, and irradiation in the presence of D_2O (5 h) did not give rise to detectable deuteration at C2.[15c,16] Furthermore, the alcohol function in **4a** could be trapped quantitatively with $Ph_2C=C=O$[1c] to give chelate **7**, with a red-shifted IR absorption for the ester carbonyl of 1630 cm^{-1}.[17]

Further studies involving ligand additions to **4a** and **5a** gave a clearer picture of the bonding and reactivity of these ketene-derived species. Bubbling CO into a solution of **5a** for 2 min produced a mixture of diasteromeric, chromatographically separable adducts **8** and **9** in a ratio of 4:1 (Scheme 1).[18] Similar treatment of enol **4a** with CO gave the adducts **10** and **11** (eq 1, ratio 3.5:1), each exhibiting a sharp singlet for the enolic proton at δ 8.33 and 5.95, respectively.[15a,19] Significantly, the isomeric enols showed very different chemical behavior. First, on saturating the solution of **10** and **11** with D_2O at room temperature, the O−H signal of the minor adduct **11** disappeared at least 100 times more rapidly than that of the major isomer **10**: times for completion were ≤5 min for **11** and 0.5 days for **10**. Second, whereas **11** tautomerized to **9** on silica gel, **10** could be isolated unchanged in 58% overall yield from **1a**. The far greater stability of **10**[20] and the downfield shift of its hydroxylic proton are both attributed to an intramolecular hydrogen bond[21ab] which based on these two criteria must be stronger in **10** than that in the five-coordinate **4a**.



(1)

We have been unable to detect **3** (Scheme 1), but it is a reasonable link between **2** and **4**: isomerization of **2a** could lead to **3a**.[22] From **3a**, enol **4a** could be produced by insertion of the ketene C=O function into the Ir−H bond. In contrast, insertion of the C=C bond into M−H bonds was reported in two intermolecular reactions,[23] where the geometric constraints of the intramolecular reaction **3** → **4** were absent. From the evidence gathered to date, the ketene functionalization represented by isomerization of **1a** to **5a** occurs by way of a four-step hydride walk, instead of by direct 1,3-hydride shift.[24]

Despite the importance of acyl ligands, and studies in the last decade on their deprotonation (ususally with strong bases),[25] the chemistry of tautomeric enol complexes involving σ-bound metal substituents[21] is virtually unexplored. The results here demonstrate for the first time in high-yield[1,9] reactions on isolable species that ketene complexes can be a source of enol and acyl[26] ligands through thermal or photochemical C−H bond activation and subsequent hydride walk.

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Supporting Information Available: Spectral data and preparations of 15 compounds (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm edition of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[13] Werner, H.; Höhn, A. *Z. Naturforsch., Teil B* **1984**, *39B*, 1505−1509.

[14] The fate of the lost elements of Ph_2C is still undetermined, but traces of two fluorescent components are seen by TLC.

[15] (a) The chemical shift of the enolic O*H* in **4a** is constant over a concentration range of 5.8−100 mM, as is the corresponding shift of the O*H* in **10** over 20−100 mM, excluding significant involvement of intermolecular hydrogen bonding. (b) For studies of sterically hindered enols, see: Hart, H.; Rappoport, Z.; Biali, S. E. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; pp 481−589. (c) Enol photochemistry: Weedon, A. C. In ref 15b, pp 591−638.

[16] Estimated lower limit of detection is 10%.

[17] For a similar observation in a crystallographically characterized chelate, see: Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669−1678.

[18] Key ^{13}C NMR data: for **8** (C_6D_6), δ 234.95 (t, $J = 8.1$ Hz, acyl C), 180.67 (t, $J = 9.3$ Hz, CO); for **9**, δ 214.03 (t, $J = 4.5$ Hz, acyl C), 177.77 (t, $J = 9.1$ Hz, CO). IR for **8**: 2004 (CO), 1665 (acyl) cm^{-1}. IR for **9**: 2023 (CO), 1640 (acyl) cm^{-1}. Assignments were fully corroborated by labeling with ^{13}CO.[8,19] At room temperature in solution, **8** isomerized to **9** (half-life ca. 30 h).

[19] ^{13}CO was added to **5a** or **4a**, giving the ^{13}CO isotopomers of **8-11**. Chelate **7** opened to a single adduct, in which the ^{13}CO and phenyl ligands were trans. Typical values for $^2J_{CC}$ across Ir in these complexes for trans- and cis-disposed carbons were 30.8−36.8 and 1.5−2.0 Hz, respectively.[8] The enolic proton resonance in the spectrum of **10**-^{13}CO appeared as a doublet ($J = 1.8$ Hz).

[20] In solution, pure **10** was consumed very slowly (~2% per day), forming **9**, whereas **11** (as a mixture with **10**) isomerized to **9** with a half-life of about a day.

[21] (a) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 3172−3177. (b) O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 4530−4544. (c) Many π-complexes of enols are known: see over 20 references in footnote 5 of ref 21b.

[22] Addition of P(*i*-Pr)$_3$ (3 equiv) did not slow the conversion of **1a** to **4a**. Possible routes from **2** to **3** and **4** could involve dissociation of the ketene C=O bond, or P(*i*-Pr)$_3$, or chloride, but present data do not allow us to distinguish rigorously between these possibilities. An intramolecular rearrangement is suggested by the observation that changing the initial concentration of **1a** by a factor of 2.8 did not change the time required to consume 90% of **1a**, and disappearance of **1a** followed first-order kinetics. We thank a reviewer for suggesting bimolecular pathways from **2** to **3**, or chloride dissociation, but the latter seems unlikely in benzene or toluene solvent.

[23] Lindner, E.; Berke, H. *Z. Naturforsch, Teil B* **1974**, *29B*, 275−276. Ungváry, F. *J. Chem. Soc., Chem. Commun.* **1984**, 824.

[24] (a) It is not known if alternative isomerization of **1** to an undetected η^2-(C,C)-bound isomer, followed by metalation at an ortho position, leads to **2**, **4**, and **5**. If metalation occurred on a C,C-bound isomer of **1**, then both **1b** and **1c** would provide the same mixture of isomeric metalation products. However, at −25 °C metalation of **1b**,**c** to **2b**,**c** is completely regiospecific. At the higher temperatures used to form **4a**, mixtures of products result from irradiation of **1b**,**c**, from equilibration between **1b**,**c** (dark reaction, 25 °C, half-life ca. 14 days; 70 °C, complete in 1 h), which is greatly accelerated on irradiation (28−30 °C, complete in 3 h). Further experiments to determine whether the metal moves by way of η^2-(C,C) or η^1-O isomers will be necessary,[24b] but based on steric considerations alone, the latter possibility is preferred. (b) Fluxionality in allene complexes: Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160−2165. In aldehyde complexes: Quirós Mendéz, M.; Seyler, J.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323−2334.

[25] Davies, S. G. *Pure Appl. Chem.* **1988**, *60*, 13−20. Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328−6343.

[26] Irradiation of the ketene complex η^2-(C,O)-[Ph(CH$_3$)C=C=O]IrCl-[P(*i*-Pr)$_3$]$_2$[6] gave thermally stable Ir(H)(Cl)[COC(Ph)=CH$_2$][P(*i*-Pr)$_3$]$_2$, whose structure is currently under investigation. Key ^{1}H NMR data: δ −11.00 (t, $J_{PH} = 10$ Hz, Ir−*H*), 6.46 (dt, $J_{PH} = 2.7$ Hz, $^2J_{HH} = 3.6$ Hz) and 4.82 (dt, $J_{PH} = 2.6$ Hz, $^2J_{HH} = 3.6$ Hz) (1 H each, C=C*H*$_2$).