Samples were sealed in 10-mL gas-tight Wheaton serum vials, deoxygenated by argon bubbling, and irradiated ≥435 nm with a 450W Xe lamp in a stirred, thermostatted rotating sample holder described elsewhere.[10] After varying degrees of photolysis, samples were centrifuged, and the supernatant was analyzed spectrophotometrically for signs of loss of free HOQ.

The performance of the different modified TiO_2 powders can be seen in Table I. HOQ-modified TiO_2 samples compare favorably with surfactant ruthenium bipyridyl modified samples, despite lower light absorption. The quantum yield, ϕ_{H_2}, expressed as moles H_2 per mole of incident (not absorbed) photons was measured for HOQ-modified TiO_2-U samples prepared as described above, but without Pt. (The active H_2-generating catalyst in this case is provided by the 0.2% RuO_2.) The spatially dispersed lines of a Coherent Radiation argon ion laser were used to irradiate vigorously stirred samples at 457.9 and 514.5 nm at intensities of 100–200 mW. The actinometer used was $Co(en)_2(SCH_2CH_2NH_2)^{2+}$ at pH 2.[11] ϕ_{H_2} was found to be 0.0034 at 457.9 nm and 0.0014 at 514.5 nm for HOQ-modified TiO_2-U. No correction was made for significant light losses due to scattering from the optically opaque suspensions, or for incomplete light absorption by the surface Ti(IV)–OQ complex. Rough correction for the expected difference in absorption by the complex at 457.9 and 514.5 nm suggests that ϕ_{H_2} is essentially the same at both wavelengths. These numbers can be compared with the value $\phi_{H_2} = 0.007$ obtained by Miller and McLendon[12] for the well-studied sacrificial system $Ru(bpy)_3^{2+}/MV^{2+}$/Pt sol/EDTA at pH 5 under conditions of essentially total light absorption. From the data in Table I, it is clear that the addition of Pt catalyst will significantly improve ϕ_{H_2} for HOQ-modified TiO_2.

Initial rates of H_2 production could be sustained for over 15 h (>40 turnovers with respect to HOQ) in samples where EDTA was replenished before the concentration dropped below 15 mM and where H_2 was regularly removed by argon purging. No loss of supernatant HOQ was observed. In samples photolyzed to extensive EDTA depletion, loss of supernatant HOQ was observed after ca. 25% loss of EDTA (assuming 2 equiv/mol); however, no drop in the rate of H_2 production was seen. Trivial blank photolysis experiments in which either HOQ or TiO_2 were omitted gave no H_2 due to the lack of light absorption. Ti(IV)–OQ complexes synthesized in nonaqueous solvents could not be used to investigate the role of bulk TiO_2 in the H_2-generating mechanism, as aqueous hydrolysis resulted in the immediate formation of TiO_2 precipitate. However, HOQ was found to form an analogous bright yellow complex with neutral Al_2O_3 chromatographic powder,[12] but this powder proved to be completely inactive when substituted for HOQ-modified TiO_2 in the H_2-generating system. This suggests that the semiconductor properties of the TiO_2 particle are involved in the function of the HOQ-modified TiO_2 in this system.

The mechanism for H_2 generation most consistent with the chemical and photophysical data presented above is one of excitation of surface Ti(IV)–OQ species, followed by charge injection into the TiO_2 particle bulk. EDTA serves to rereduce the oxidized surface species before decomposition occurs,[13] while the electron is channeled to a Pt or RuO_2 catalyst deposit on the particle where reduction of H^+ takes place. We have found preliminary evidence for photosensitized charge injection in photoelectrochemical cells containing HOQ-modified polycrystalline TiO_2 electrodes[14] and are presently pursuing this investigation in depth. The extention of this work to other dye analogues capable of absorbing more of the solar spectrum is an obvious one, and as such, HOQ-modified TiO_2 represents a prototype system of great importance in the field of photochemical conversion research.

Acknowledgment. We are grateful to Dr. Enrico Borgarello for his contribution of technical advice and to Dr. Thomas Geiger for performing electrochemical measurements. This work was supported by the Swiss National Fund for Scientific Research and by the RE Foundation, Zürich.

Registry No. 8-Hydroxyquinoline, 148-24-3; anatase, 1317-70-0; platinum, 7440-06-4; ruthenium dioxide, 12036-10-1; hydrogen, 1333-74-0; water, 7732-18-5; EDTA, 60-00-4.

Supplementary Material Available: Graph of photocurrent from HOQ-modified polycrystalline TiO_2 electrode (1 page). Ordering information is given on any current masthead page.

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[10] Houlding, V. H.; Geiger, T.; Kölle, U.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1982**, 681–683. Because the samples are rotated through the light path, the incident light is less than for direct irradiation.

[11] Houlding, V. H.; Mäcke, H.; Adamson, A. W. *Inorg. Chem.* **1981**, 20, 4279–4285.

[12] Baker alumina (stock no. 0537) was used (surface area 220 m^2/g by BET), and approximately 1 mequiv/g HOQ was adsorbed onto the surface. This does not correspond to saturation of the surface. Pt sol was deposited in a manner analogous to the TiO_2 samples, and centrifugation revealed no residual Pt in solution.

[13] Cyclic voltammetric studies of HOQ at pH 7.0 (conditions: 1 mM HOQ, 0.2 M KCl, phosphate buffer, basal plane graphite electrode vs. Ag/AgCl, scan rate 0.1 V/s) showed that both one-electron oxidation and reduction gave species that were chemically unstable. On the first anodic scan, oxidation occurred with E_{pa} 0.48 V, and the rereduction peak was minimal. The first cathodic scan showed a reduction at E_{pc} −1.1 V with no corresponding reoxidation wave. Subsequent scans were seriously distorted with respect to first scans. See also: Claret, J.; Muller, C.; Feliu, J. M.; Virgili, J. *Electrochim. Acta* **1982**, *27*, 1475–1479.

[14] Desilvestro, J.; Houlding, V. H.; Grätzel, M., to be published.

Carbon Monoxide Activation by Organoactinides. η^2-Acyl–CO Coupling and the Formation of Metal-Bound Ketenes

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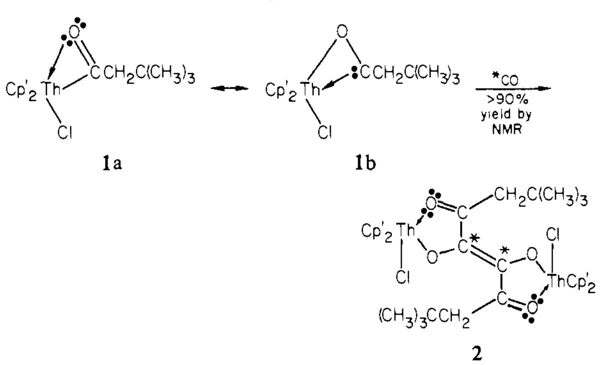
The coupling of metal carbenes (and carbynes) with CO to yield coordinated ketenes is a well-documented process.[1] We recently reported that the thorium acyl complex $Cp'_2Th[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ (**1**, Cp′ = $\eta^5\text{-}(CH_3)_5C_5$) reacts with CO to yield the unusual dionediolate **2** (eq 1).[2] On the basis of ^{13}C labeling



1a **1b**

2

(1)

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[1] (a) Brown, T. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122 and references therein. (b) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (c) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, 1255–1256. (d) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133–3135. (e) Herrmann, W. A.; Plank, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525–526. (f) Redhouse, A. D.; Herrmann, W. A. *Ibid.* **1976**, *15*, 615–616. (g) Kreissl, F. R.; Eberl, K.; Nedelhoven, W. *Chem. Ber.* **1977**, *110*, 3782–3791. (h) Dorrer, B.; Fischer, E. O. *Ibid.* **1974**, *107*, 2683–2690.

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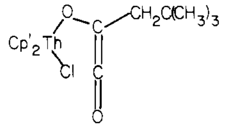
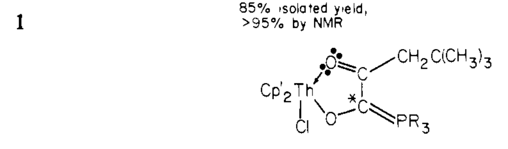
experiments, it was tentatively suggested that a crucial step in product formation was coupling of the carbene-like[3] (**1b**) dihaptoacyl with CO to produce a transitory ketene (e.g., **3**). If



3

operative, such a pathway would represent a new pattern of acyl reactivity, also of possible importance in actinide and zirconium enediolate formation[4] as well as in organolanthanide carbonylation chemistry.[5] We report here mechanistic evidence that such η^2-acyl–CO coupling processes are indeed facile.

In the presence of >1 equiv of PR_3 ($R = C_6H_5$, CH_3), acyl complex **1** reacts with carbon monoxide to form the ylides **4a**,**b** in high yield (eq 2). These new complexes were characterized



(2)

4a, $R = C_6H_5$; 4a*, $^*C = {}^{13}C$
4b, $R = CH_3$

by standard methods.[6] The ^{31}P chemical shifts of **4a**,**b** appear at δ −1.8 and 2.30 ppm, respectively, and **4a*** exhibits δ ^{13}C for *C at 117.8 and $^1J_{PC} = 123$ Hz; these parameters compare favorably with those of known ylides.[7]

Single crystals of **4b** were obtained by allowing CO to slowly diffuse into a solution of **1** and $P(CH_3)_3$ in toluene at 0 °C. At 20 ± 1 °C, they are monoclinic, space group $P2_1/n$ (a special setting of $P2_1/c$-C_{2h}^5, No. 14) with $a = 15.152$ (3) Å, $b = 20.442$ (7) Å, $c = 10.354$ (3) Å, $\beta = 92.08$ (2)°, $Z = 4$ [μ_a(Mo K$\bar{\alpha}$) = 4.97 mm^{-1}; $d_{calc} = 1.536$ g cm^{-3}].[8] Three-dimensional X-ray diffraction data were collected for 7354 independent reflections having $2\theta_{Mo K\bar{\alpha}} < 55°$ (the equivalent of 1.0 limiting Cu K$\bar{\alpha}$ sphere) on a Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (0.90° wide) ω scans. The structure was solved using the "heavy-atom" technique. The resulting structural parameters have been refined to convergence [R (unweighted, based on F) = 0.051 for 4213 independent absorption-corrected reflections having $2\theta_{Mo K\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$] by using empirically weighted full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed on a Data General Eclipse S-200 computer using local versions of the Nicolet EXTL software system.

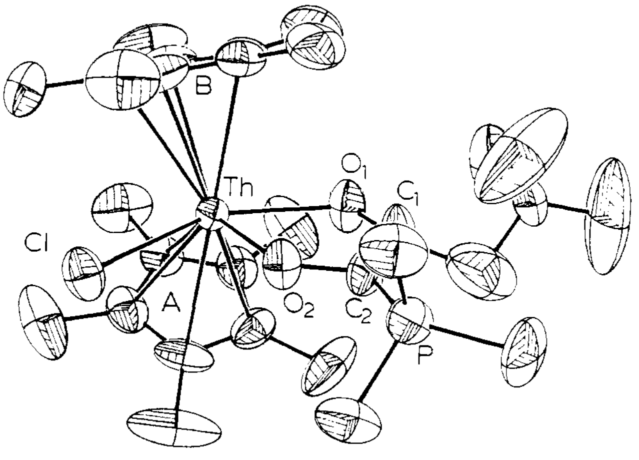
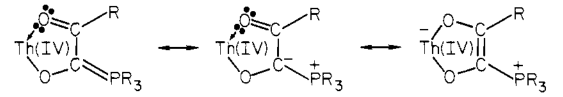


Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms in Th[η^5-$(CH_3)_5C_5$]$_2$(Cl)O_2C_2[$CH_2C(CH_3)_3$][$P(CH_3)_3$] (**4b**). All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Important bond lengths (Å) and angles (deg) for chemically distinct groups of atoms are: Th–O_1 = 2.340 (9), Th–O_2 = 2.256 (8), Th–Cl = 2.753 (4), C_1–O_1 = 1.33 (2), C_2–O_2 = 1.36 (2), C_1–C_2 = 1.36 (2), C_2–P = 1.73 (1), P–C(methyl) = 1.79 (2, 1, 2, 3) Å, O_1–Th–O_2 = 67.4 (3)°, O_2–Th–Cl = 78.3 (2)°, C_1–O_1–Th = 119.2 (9)°, C_2–O_2–Th = 120.1 (7)°, (ring center of gravity)–Th–(ring center of gravity) = 133.6°. The Th, P, and neopentyl methylene carbon atoms are displaced from the $O_1C_1C_2O_2$ least-squares mean plane by +0.22, −0.11, and +0.62 Å, respectively.

As shown in Figure 1,[9] the thorium ion in **4b** is formally 9-coordinate, with the $Cp'_2M(X)(Y)(Z)$ coordination geometry observed in **1**,[2] **2**,[2] and $Cp'_2U[(CH_3)_2PCH_2CH_2P(CH_3)_2]H$.[10] The Cp'_2Th metrical parameters are unexceptional,[2,3,11] while the Th–O contacts, 2.340 (9) and 2.256 (8) Å, are longer than in $(Cp'_2Th)_2[\mu$-$O_2C_2(CH_3)_2]_2$ (2.154 (8, 2, 2, 2) Å)[9,11b] and more symmetrical than in **2** (2.53 (1), 2.27 (1) Å).[2] This result, the apparently long C–O contacts (1.33 (2), 1.36 (2) Å),[12] and the apparently short C_1–C_2 distance (1.36 (2) Å)[12] suggest the importance of resonance hybrid C. The P–C_2 distance of 1.73 (1) Å appears to be only slightly shorter than the average P–C(methyl) distance of 1.79 (2, 1, 2, 3) Å[9] and is consistent with structures of more typical ylides.[12,13]



A B C

Kinetic studies were undertaken to ascertain whether **4** might be a phosphine-trapping product of **3** since ketenes are known to suffer nucleophilic attack at the α carbon atom.[14] The rate of

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[2] Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396.

[3] (a) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989–997. (b) Fagan, P. J.; Maatta, E. A.; Marks, T. J. *ACS Symp. Ser.* **1981**, *No. 152*, 52–78.

[4] (a) Katahira, D. A.; Moloy, K. G.; Marks, T. J. In "Advances in Catalytic Chemistry"; Hanson, F. V., Ed.; Plenum Press: New York; Vol. II, in press. (b) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723–1726. Recent kinetic evidence precludes the intermediacy of ketenes in the enediolate-forming carbonylation of thorium formyls. (c) Moloy, K. G.; Marks, T. J. presented in part at "Inorganic Chemistry: Towards the 21st Century", Bloomington, IN, May 16–19, 1982. (d) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127.

[5] Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706–708.

[6] All new compounds gave expected spectral and analytical data; see supplementary materials for details.

[7] (a) Gray, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 5092–5094. (b) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 1–489. (c) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper and Row: London, 1976; pp 82, 274–275. (d) Grim, S. O.; McFarlane, W.; Marks, T. J. *J. Chem. Soc., Chem. Commun.* **1967**, 1191–1192.

[8] Corresponding lattice constants for the $P2_1/c$ description of the unit cell are: $a = 10.354$ (3) Å; $b = 20.442$ (7) Å; $c = 18.040$ (5) A; $\beta = 122.92$ (3)°.

[9] The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

[10] Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 865–867.

[11] (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357–7360. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *Ibid.* **1981**, *103*, 2206–2220. (c) Marks, T. J.; Manriquez, J. M.; Fagan, P. J.; Day, V. W.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *No. 131*, 1–29.

[12] (a) C–O = 1.428 (5) Å (CH_3OH); C–O = 1.214 (5) Å, C–C = 1.501 (5) Å (CH_3CHO); C–C = 1.534 (5) Å (C_2H_6); C–C 1.337 (5) Å (C_2H_4); C–P = 1.841 (5) Å ($P(CH_3)_3$).[12b] (b) *Spec. Publ.-Chem. Soc.* **1965**, *18*, M665.

[13] Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350–365 and references therein.

[14] Black, P. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley-Interscience: New York, 1980; Chapter 9, pp 309–342.

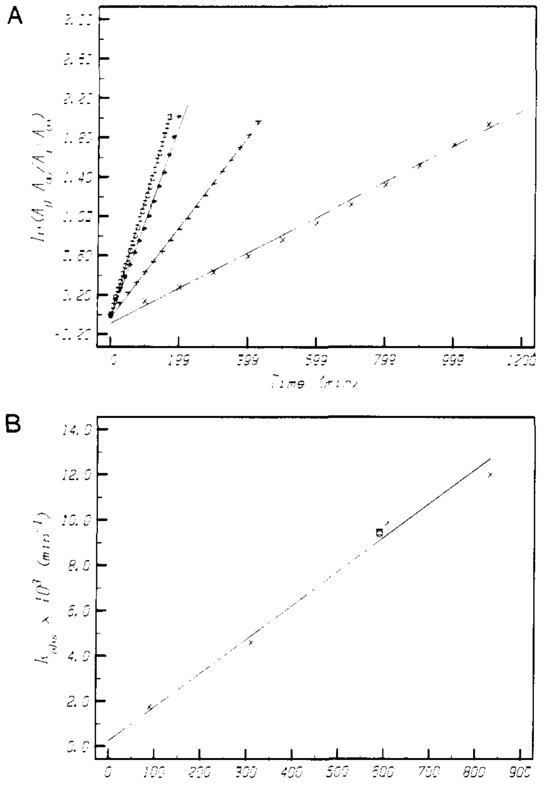
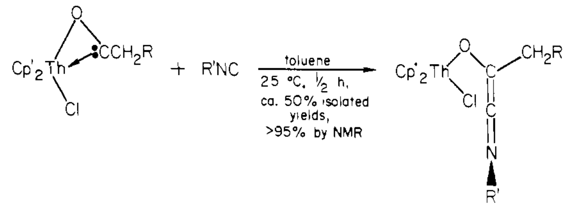


Figure 2. (A) Kinetic plots for the reaction of **1** with CO in the presence of excess $P(CH_3)_3$ at various CO pressures: □, 831 torr; *, 606 torr; +, 310 torr; ×, 89 torr. (B) Dependence of the observed rate constant on CO pressure: x, **1** + excess $P(CH_3)_3 \rightarrow$ **4b** in THF; □, **1** + excess $P(C_6H_5)_3 \rightarrow$ **4a** in toluene; O, **1** → **2** in toluene. From these data, velocity = $k[\mathbf{1}]P_{CO}$ where $k = 1.50\ (5) \times 10^{-5}$ min^{-1} torr.$^{-1}$.

1 → **2**, **4a**, or **4b** at 30.8 ± 0.05 °C was measured manometrically by CO uptake or spectrophotometrically by monitoring the disappearance of the 420-nm band of **1** ($\epsilon = 1.35 \times 10^2$ cm^{-1} M^{-1}). A large gas volume and efficient mixing ensured pseudo-first-order conditions in CO[15] for each determination. The reaction at a given CO pressure (P_{CO}) is first order in **1** over 3–4 half-lives and a 9–10-fold range in P_{CO} (and, therefore, [CO] assuming Henry's law is obeyed) (Figure 2A). Furthermore, the observed rate constants are linear in P_{CO} (Figure 2B), implying first-order dependence on CO. Additional experiments demonstrate that, for identical P_{CO}, the rates of eq 1 and 2 are indistinguishable and that the observed rates are independent of phosphine ($P(CH_3)_3$ or $P(C_6H_5)_3$) and solvent (THF or toluene). Finally, no intermediates were detected when the reaction was monitored by ^{1}H NMR or IR (2500–1500 cm^{-1}). These data argue that the rate-limiting step in eq 1 and 2 is the coupling of η^2-acyl with CO to produce ketene **3** (or a short-lived species that reacts as or rearranges to **3**), which then proceeds rapidly to **2** (possibly by dimerization[16]) or is trapped[17] by phosphine.

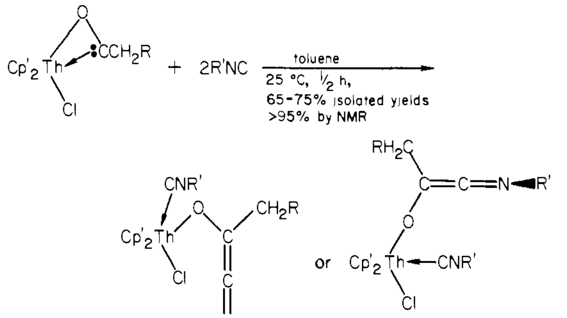
Further support for facile η^2-acyl–CO coupling is derived from studies with isoelectronic isocyanides. The reaction of **1** or $Cp'_2Th(\eta^2\text{-}COCH_2C_6H_5)Cl$ with isonitriles (eq 3) produces



(3)

5a, $R = C(CH_3)_3$; $R' = C(CH_3)_3$
5b, $R = C_6H_5$; $R' = C(CH_3)_3$
5c, $R = C(CH_3)_3$; $R' = C_6H_{11}$

ketenimines **5a–c**.[18] With 2 equiv of RNC, adducts **6a–c** are obtained (eq 4). All spectroscopic and analytical data support



(4)

6a, $R = C(CH_3)_3$; $R' = C(CH_3)_3$
6b, $R = C_6H_5$; $R' = C(CH_3)_3$
6c, $R = C(CH_3)_3$; $R' = C_6H_{11}$

a ketenimine formulation.[6] Thus, **5a–c** and **6a–c** exhibit a strong band at ca. 2000 cm^{-1} in the infrared attributable to ν_{CCN}.[19] Also, **6a–c** exhibit a ν_{CN} transition ca. 30 cm^{-1} above that of the free isocyanide, consistent with coordination to an f^0 center.[20] In the ^{1}H NMR spectra, all methylene and Cp′ protons appear as diastereotopic pairs, reflecting the asymmetric nature of the ketenimine functionality.[21] The precise disposition of ligands in **6a–c** cannot be deduced from the data at hand. However, one of the $Cp'_2Th(X)(Y)(Z)$ structures in eq 4 appears most reasonable. The unperturbed character of the ketenimine vibrations in **5a–c** and their insensitivity to isonitrile coordination (cf. **6a–c**) appear to preclude coordination of the cumulene moiety to thorium via the nitrogen lone pair or π system. This apparently reflects unfavorable steric interactions between bulky R′ and Cp′ groups (not present in **2**) and may explain why **5a–c** do not form products analogous to **2**.

These $Th(\eta^2\text{-}COR)$–CO homologation results further underscore the "anchored" Fischer carbene-like character of actinide dihaptoacyls. They also suggest new avenues for C=C bond formation which are under further investigation.

Acknowledgment. We thank the National Science Foundation (CHE8009060) for generous support of this research.

Supplementary Material Available: Spectroscopic and analytical data for new compounds, a table of fractional atomic coordinates (Table I), and a table of anisotropic thermal parameters (Table II) for non-hydrogen atoms of $Th[\eta^5\text{-}(CH_3)_5C_5]_2(Cl)O_2C_2[CH_2C(CH_3)_3][P(CH_3)_3]$ (**4b**) (6 pages). Ordering information is given on any current masthead page.

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[15] Gjaldbaek, J. C.; Andersen, E. K. *Acta Chem. Scand.* **1965**, *8*, 1398–1413 (CO solubilities).

[16] This question is under continuing investigation.

[17] The course of eq 1 is diverted by neither *trans*-$(C_6H_5)HC{=}CH(C_6H_5)$ (2–3 equiv) nor $(CH_3)_2C{=}C(CH_3)_2$ (neat), arguing against intermediates such as[16]

[18] For what may be a similar reaction involving iminoacyls, see: Yamamoto, Y.; Yamazaki, H. *J. Organomet. Chem.* **1975**, *90*, 329–334; *Inorg. Chem.* **1974**, *13*, 438–446.

[19] Barker, M. W.; McHenry, W. E. "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley-Interscience: New York, 1980; Chapter 17, pp 701–720.

[20] Goffart, J. In "Organometallics of the f-Elements"; Marks, T. J., Fischer, R. D., Eds.; Reidel: Dordrecht, Holland, 1979; Chapter 15, pp 482–483.

[21] Anet, F. A. L.; Jochims, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 5524–5524 and references therein. Inversion rates at ketenimine nitrogen centers are strongly sensitive to substituents.