CH_3CH_2OCO, R_2 = $CH{=}C(CN)_2$; n = 11), 87280-73-7; **13** (R_1 = HOOC, R_2 = CHO; n = 9), 87280-68-0; **13** (R_1 = HOOC, R_2 = CHO; n = 10), 87280-69-1; **13** (R_1 = HOOC, R_2 = CHO; n = 11), 87280-70-4; **14** (R_1 = H, R_2 = CHO; n = 9), 87280-65-7; **14** (R_1 = H, R_2 = CHO; n = 10), 87280-66-8; **14** (R_1 = H, R_2 = CHO; n = 11), 87280-67-9; **15**, 87280-62-4; **16** (n = 9)·2MeOH·$x$$ClCH_2Cl$, 87280-59-9; **16** ($n$ = 9), 87280-58-8; **16** (n = 10), 87280-60-2; **16** (n = 11), 87280-61-3; nonanedioyl dichloride, 123-98-8; decanedioyl dichloride, 111-19-3; undecanedioyl dichloride, 45165-01-3; 2,12-diethyl-3,7,13,17-tetramethyl-8,18-(decamethylene)-5,15-dihydroporphyrin, 87280-63-5; 2,12-diethyl-3,7,13,17-tetramethyl-8,18-(undecamethylene)-5,15-dihydroporphyrin, 87280-64-6.

Supplementary Material Available: Table I listing average bond distances, Table II listing the thermal parameters, and Table III listing the final positional parameters are available for compound **16**, n = 9 (6 pages). Ordering information is given on any current masthead page.

Uranium–Carbon Multiple Bond Chemistry. 2. Coupling of Bridging and Terminal Carbonyls to an Iron η^1:η^3-Allyl Complex[1]

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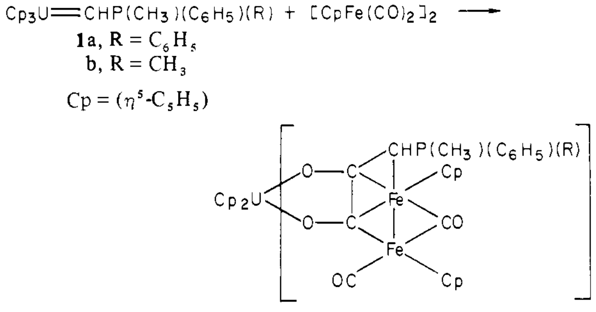
Received March 21, 1983

The coupling of carbon monoxide molecules is of significance in both synthetic and catalytic organometallic chemistry.[2-11] We have demonstrated that the uranium–carbon multiple bond in $Cp_3U{=}CHPR_3$ reacts with polar, unsaturated systems including carbon monoxide.[1,12] In this communication we report its reaction with $[CpFe(CO)_2]_2$, in which coupling of bridging and terminal carbonyls occurs and a new carbon–carbon bond forms between carbonyl and ylide moieties. Apparently carbon–carbon coupling does not occur by any of the usual, well-documented C–C bond-forming processes.[2-11]

The reaction of equimolar quantities of $Cp_3U{=}CHP(CH_3)(C_6H_5)R$ (**1**) and $[CpFe(CO)_2]_2$ in THF at 25 °C under nitrogen for 8 h produced dark green crystals (**2**) in 45% yield based on phosphorus (eq 1). Cp_4U, identified by NMR, and other incompletely characterized paramagnetic species remain in solution. The ^1H NMR spectra, summarized in Table I, supplementary material, of **2** contain three singlet resonances due to Cp groups, one of which can be assigned as Cp bound to U and the other two as nonequivalent CpFe groups. Additional resonances can be attributed to $CHP(CH_3)(C_6H_5)(R)$ fragments. The infrared spectra of **2a** and **2b** (Table II, supplementary material) contain bands due to both terminal and bridging carbonyls. These data do not provide sufficient information to characterize **2**, thus an X-ray diffraction study was undertaken.

Structures of both **2a** and **2b** were determined and crystal parameters are summarized in Table III, supplementary material.



1a, R = C_6H_5
b, R = CH_3
Cp = (η^5-C_5H_5)

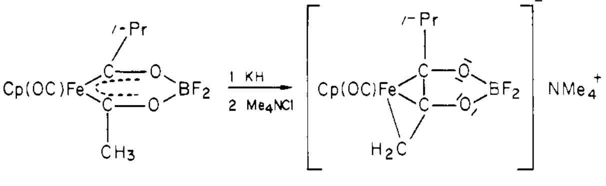
(1)

2a, R = C_6H_5
b, R = CH_3

With the obvious exception of the R group attached to phosphorus, the structures of **2a** and **2b** are very similar. Since a disorder problem exists within one allyl ligand in **2a**, while **2b** is well-behaved, the structural data discussed below are from **2b**.

The molecular structure of **2b** is shown in Figure 1, while structural parameters are summarized in Tables IV and V, supplementary material. The 2.544 (5)-Å Fe(1)–Fe(2) bond length in **2** is very close to the 2.531 (2) Å observed for the Fe–Fe bond in *cis*-$[CpFe(CO)_2]_2$.[13] The distances, C(12)–C(11), 1.34 (3) and, C(11)–C(15), 1.42 (3) Å in the complex organometallic ligands coordinated to Cp_2U are shorter than expected for C–C single bonds, and are consistent with an allyl group. As expected for a delocalized π system the atoms C(11), C(12), and C(15) and their substituents, O(11), O(12), and P and Fe(2), are planar. The distances, Fe(1)–C(11), 2.13 (2), Fe(1)–C(12), 2.05 (2), and Fe(1)–C(15), 2.08 (2) Å are typical for iron η^1:η^3-allyl complexes,[14] and Fe(1) is located 1.46 Å below the allyl plane. The Fe(2)–C(12) distance, 1.96(2) Å, is typical of an η^1 iron vinylcarbene bond.[14] Thus, each of the organoiron ligands derived from a $[CpFe(CO)_2]_2$ molecule contains a newly formed η^1:η^3-allyl created by bond formation between a carbonyl group bonded to iron and $CHPR_3^-$ plus coupling of bridging and terminal carbonyls in the iron dimer.

The mechanism for formation of **2** has not been determined. However, insertion of a terminal carbonyl of $[CpFe(CO)_2]_2$ into the uranium–carbon bond of **1** would be consistent with the known chemistry of **1**.[1,12] The resulting iron enolate carbene intermediate, complex A in Scheme I, could rearrange to B and then undergo ligand exchange to form **2** and Cp_4U. The formation of A and its conversion to B is consistent with the affinity of U(IV) for oxygen,[15] the ability of Cp_3UX compounds to complex hard bases,[16] and the activation of coordinated carbon monoxide by interaction with hard Lewis acids.[17,18] Significantly, the proposed conversion of A to B also closely resembles the transannular coupling that occurs in the reduction of an iron diketonate[19] (eq 2), and similar intermediates can be drawn for both coupling reactions.[20]



(2)

3

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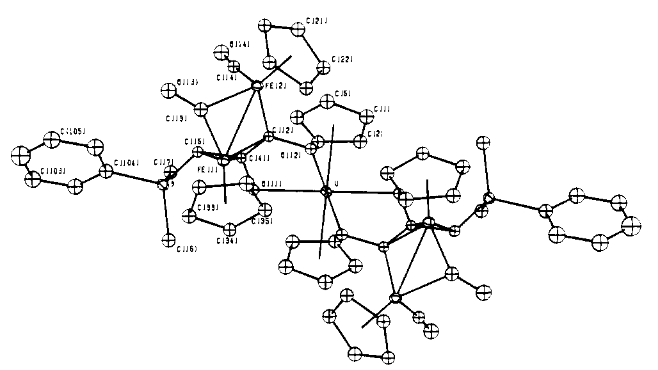
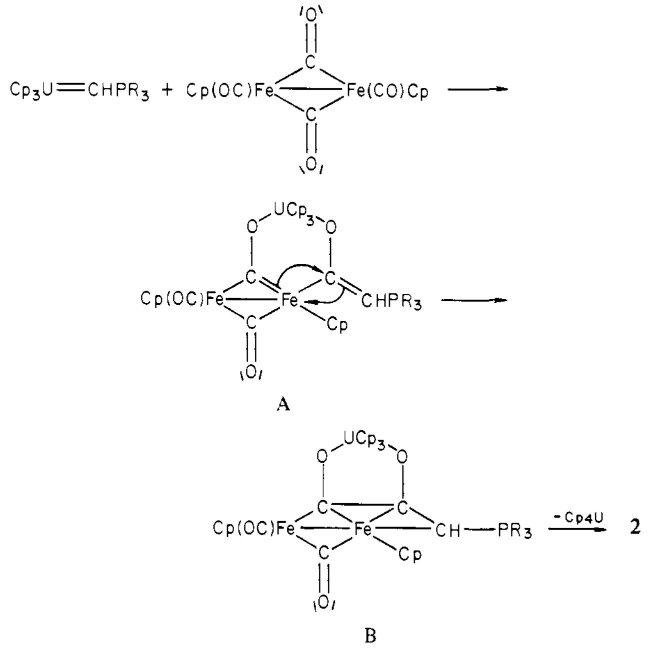
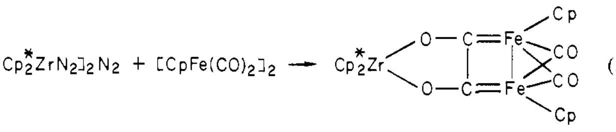


Figure 1. Labeled, perspective ORTEP view of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$.

Scheme I



Carbon monoxide coupling in early transition metal carbonyls is unusual. The single other well-documented example is the recently reported reaction (eq 3),[21] which also involves carbonyl



4

$Cp^* = (CH_3)_5C_5^-$

coupling in $[CpFe(CO)_2]_2$; however, important differences exist between **2** and **4**. Formation of **2** (eq 1) involves the formation of two new C-C multiple bonds to produce an η^1:η^3-allyl. Uranium(IV) is present at the beginning and end of the reaction. In contrast, in **4** one new C-C single bond has formed, Zr(II) has been oxidized to Zr(IV), and **4** is a Fischer type dicarbene complex. The fact that CO coupling can produce two dissimilar products from the same metal carbonyl indicates that direct CO coupling is a versatile reaction pathway.

Acknowledgment. The support of this work by the National Science Foundation, Grant CHE-8210244 to J.W.G. and R.E.C., is gratefully acknowledged.

Supplementary Material Available: Table I, nuclear magnetic resonance data; Table II, infrared spectral data; Table III, summary of crystal data; Table IVa, interatomic distances of $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table IVb, interatomic distances of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$; Table Va, bond angles of $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table Vb, bond angles of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$; Table VIa, positional and thermal parameters for $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table VIb, positional and thermal parameters for $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$; Table VIIa, listing of $10|F_o|$ vs. $10|F_c|$ of $Cp_2U[(O_2C_2CHP(CH_3)(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$; Table VIIb, listing of $10|F_o|$ vs. $10|F_c|$ of $Cp_2U[(O_2C_2CHP(CH_3)_2(C_6H_5))Fe_2Cp_2(CO)_2]_2$ (37 pages). Ordering information is given on any current masthead page.

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Coupling of Alkenes with Fischer-Type Alkylidene Complexes of Iron

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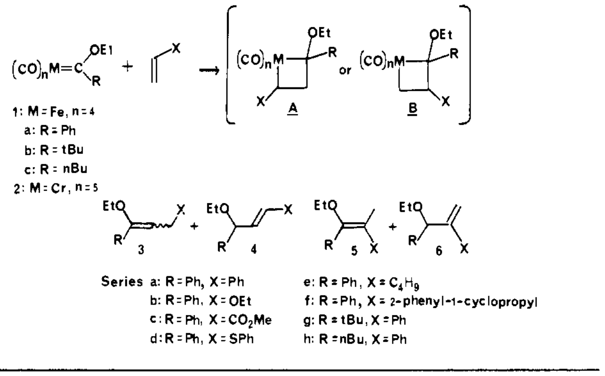
A general method of preparation of (ethoxyalkylidene)tetracarbonyliron(0) complexes[1,2] (**1**) makes possible the first inquiry into their chemical reactivity.[5] In this paper, we report the generality of a new carbon-carbon coupling reaction of functionalized alkenes with **1a-c**. The reaction proceeds with high regioselectivity, and we report preliminary experiments that probe the nature of the intermediates. It was demonstrated that the chromium analogues (**2**) react with polarized alkenes (acrylates, vinyl ethers) to generate cyclopropanes and alkene metathesis products, processes that can be written via metallacyclobutanes (A and B).[6] Rearrangement to coupling products **3** and**4** (from **A**) and **5** and **6** (from **B**) can also be written, but has hitherto not been observed with Fischer-type alkylidene complexes.[7]



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[2] Complexes of type **1** have been characterized in special cases;[3,4] we are unaware of examples of their chemical reactivity.

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[7] No *functionalized* alkene has been reported to give products such as **3-6** with alkylidene-metal complexes of any sort. However, a few isolated examples have been noted with simple alkenes. The coupling of alkylidene-tantalum and -niobium complexes with styrene and *tert*-butylethylene to produce homologous alkenes has been observed: McLain, S. M.; Wood, C. D.; Shrock, R. R. *J. Am. Chem. Soc.* **1977**, *95*, 3519-3520. The alkylidene complexes of niobium and tantalum complexes show polarization of the alkylidene carbon opposite of that of the Fischer-type alkylidene complexes, and the pathways may be quite different. Shrock et al. postulate an intermediate metallacyclobutane and rearrangement to the alkene, with regioselectivity controlled by the polarization in the alkylidene complex.

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