photoproduct definitively, we have carried out exhaustive bulk photolyses. $[PdX(CNCH_3)_3]PF_6$[38] (X = Cl, Br) is the sole product obtained from photolyzed solutions containing CCl_4 or CBr_4, respectively, based on IR, NMR, and microanalytical data.[42] The halogen abstraction must proceed by a photochemical pathway. We see no evidence for a thermal reaction between $[Pd_2{}^{I}(CNCH_3)_6]\cdot 2(PF_6)$ and CCl_4 when solutions identical with those used in the photochemical studies are refluxed for up to 6 h. We do, however, observe a slow thermal reaction between 1 and CBr_4 under the same conditions.

The participation of $\cdot Pd^{I}(CNCH_3)_3{}^{+}$ radicals in the observed photochemistry is strongly suggested by the results of a cross-coupling experiment. Photolysis of a mixture of the two homonuclear dimers $[Pd_2{}^{I}(CNCH_3)_6]\cdot 2(PF_6)$ and $[Pt_2{}^{I}(CNCH_3)_6]\cdot 2(PF_6)$[38] gives the heteronuclear $[PdPt(CNCH_3)_6]\cdot 2(PF_6)$.[38] This photochemical cross-coupling reaction is conveniently monitored by ^{195}Pt NMR spectroscopy. The platinum dimer, $[Pt_2{}^{I}(CNCH_3)_6]\cdot 2(PF_6)$ exhibits a ^{195}Pt NMR signal at δ −2916 relative to K_2PtCl_4. The mixed-metal dimer $[PdPt(CNCH_3)_6]\cdot 2(PF_6)$ has been independently prepared by an established chemical synthesis,[38] and it exhibits a ^{195}Pt NMR signal at δ −2833 relative to K_2PtCl_4. Significantly, the photolysis of an equimolar mixture of the two homonuclear dimers in acetonitrile solutions is accompanied by loss in intensity at δ −2916 and concomitant increase in intensity at δ −2833 relative to K_2PtCl_4. Similarly, irradiation of solutions originally containing only the mixed-metal dimer $[PdPt(CNCH_3)_6]\cdot 2(PF_6)$ cleanly yields homonuclear $[Pt_2(CNCH_3)_6]\cdot 2(PF_6)$, as evidenced by the growth of a ^{195}Pt signal at δ −2916. These results suggest that $\cdot Pd^{I}(CNCH_3)_3{}^{+}$ and $\cdot Pt^{I}(CNCH_3)_3{}^{+}$ radical fragments are formed upon photochemical homolysis of Pd–Pd, Pt–Pt, and Pd–Pt bonds in the dimetallic hexakis(isocyanide) complexes used in this study and that the lifetimes of these radicals are sufficient for cross coupling between dimers to occur. The cross-coupling experiments have also been followed by ^{1}H NMR spectroscopy at 200 MHz of the isocyanide methyl resonances. The results of our ^{1}H NMR studies entirely support the ^{195}Pt NMR data, and further details will be provided in the full paper. We note that all cross-coupling photolyses were done at 0 °C and that no evidence for thermal cross coupling at 25 °C is observed over periods of weeks.

The efficiencies for halogen atom abstractions by photogenerated $\cdot Pd^{I}(CNCH_3)_3{}^{+}$ radicals are high. Quantum yields for disappearance of $[Pd_2(CNCH_3)]\cdot 2(PF_6)$, $\Phi_{dis_{313}}$, are 0.42 ± 0.1 and 0.70 ± 0.1 for reactions with CCl_4 and CBr_4, respectively (eq 1). The high quantum yields for

$$\underset{\mathbf{1}}{[Pd_2{}^{I}(CNCH_3)_6]\cdot 2(PF_6)} + CX_4 \xrightarrow[CH_3CN]{\lambda\ 313\ nm} \begin{array}{c} [Pd^{II}X(CNCH_3)_3]PF_6 \\ \mathbf{2},\ X = Cl,\ \Phi_{dis} = 0.42 \pm 0.1 \\ \mathbf{3},\ X = Br,\ \Phi_{dis} = 0.70 \pm 0.1 \end{array} \quad (1)$$

halogen atom abstraction suggest the efficient homolysis of the Pd–Pd bond is responsible for the observed photochemistry. An important line of investigation therefore is the direct observation of $\cdot Pd^{I}(CNR)_3{}^{+}$ radicals obtained by homolysis of the Pd–Pd bond in 1. UV photolysis of frozen acetonitrile solutions of 1 in an EPR cavity at 150 K causes the appearance of an intense EPR signal with an apparent g_{iso} = 2.12, consistent with a metal-based radical. The signal is quenched by melting the matrix or discontinuing photolysis. The EPR results provide additional support for the notion that photochemical Pd–Pd bond homolysis of 1 precedes the observed halogen atom abstraction photochemistry.

Our results suggest that photolysis of 1 leads to homolysis of the Pd^{I}–Pd^{I} bond to give two 15-electron d^9 $\cdot Pd^{I}(CNCH_3)_3{}^{+}$ fragments which are capable of reacting in a one-electron sense with halocarbons to give $Pd^{II}X(CNCH_3)_3{}^{+}$. The photogeneration of reactive organometallic fragments has recently found application in the activation of aliphatic C–H bonds.[44] Reactive photogenerated species such as $\cdot Pd^{I}(CNR)_3{}^{+}$ may find significant applications in the activation of small molecules or C–H bonds. Further studies in these laboratories are being conducted along these lines. In particular, the 15 valence electron species $\cdot Pd^{I}(CNCH_3)_3{}^{+}$ has the clear potential to participate in three-electron activations of substrates such as allylic systems, NO, and alkylidynes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. This work was also supported in part by the Purdue Research Foundation. The assistance of Mr. John Copeland in the design and construction of the medium-pressure mercury lamp and the assistance of Mr. William Kennedy in obtaining EPR spectra of UV photogenerated radicals are gratefully acknowledged. The experimental assistance of Mr. David Whittern in obtaining the ^{195}Pt NMR and 200-MHz ^{1}H NMR spectra is also gratefully acknowledged. The Varian XL-200 spectrometer was purchased with funds from NSF Grant CHE-8004246. This support is gratefully acknowledged.

Registry No. 1, 56116-48-4; 2, 69108-81-2; 3, 69108-67-4; $[PdPt(CNCH_3)_6]\cdot 2(PF_6)$, 60767-38-6; Pd, 7440-05-3.

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(42) **$[Pd^{II}Cl(CNCH_3)_3]PF_6$**: IR ν(CN) 2284 cm^{-1} (CH_2Cl_2); ^{1}H NMR $\delta(CH_3)$ 3.49, (s, CD_3CN). Anal. Calcd: C, 17.56; H, 2.19; N, 10.25. Found: C, 17.80; H, 2.21; N, 10.35.

$[Pd^{II}Br(CNCH_3)_3]PF_6$: IR ν(CN) 2278 cm^{-1} (CH_2Cl_2); ^{1}H NMR $\delta(CH_3)$ 3.39, (s, CD_3CN). Anal. Calcd: C, 15.85; H, 1.98; N, 9.26. Found: C, 16.04; H, 2.02; N, 9.38.

(43) Quantum yields were measured at 313 nm by ferrioxalate actinometry or by direct comparison with 0.01 M $Mn_2(CO)_{10}$ in neat CCl_4 solution assuming $\Phi_{dis_{313}}$ = 0.48.[11]

(44) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1982, *104*, 352.

Organic Sonochemistry. Ultrasonic Acceleration of the Hydrosilation Reaction[1]

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Summary: Sonic waves permit the platinum-catalyzed addition of Si–H bonds across C=C and C≡C bonds at ~30 °C in high yields.

The first examples of platinum-catalyzed hydrosilations were described by Wagner and Strother.[2] In that work the addition reactions were performed at 45–115 psi at temperatures of 100–300 °C using, in most cases, trichlorosilane, as well as dichlorosilane, triethoxysilane, and ethyldichlorosilane, on a series of terminal alkenes. Subsequent work by Wagner and others demonstrated that heterogeneous platinum catalysts accelerated a variety of

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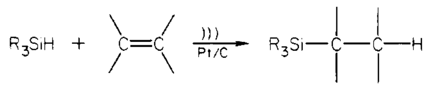
Table I. Sonically Accelerated Hydrosilation Reactions[a]

reaction no.	alkene	silane	time, h	product	yield,[b] %
1	1-hexene	$HSiCl_3$	1	n-$C_6H_{13}SiCl_3$	90
2		$HSiMeCl_2$	1	n-$C_6H_{13}SiMeCl_2$	95
3		$HSiEt_3$	2	n-$C_6H_{13}SiEt_3$	74
4	4-methyl-1-pentene	$HSiCl_3$	1	$(CH_3)_2CHCH_2CH_2CH_2SiCl_3$	94
5		$HSiMeCl_2$	1	$(CH_3)_2CHCH_2CH_2CH_2SiMeCl_2$	96
6		$HSi(OEt)_3$	1	$(CH_3)_2CHCH_2CH_2CH_2Si(OEt)_3$	93
7	styrene	$HSiCl_3$	1.5	$PhCH_2CH_2SiCl_3$	94
8		$HSiMeCl_2$	1.5	$PhCH_2CH_2SiMeCl_2$	94
9	2-methyl-1-pentene	$HSiCl_3$	2	$CH_3CH_2CH_2CH(CH_3)CH_2SiCl_3$	71
10		$HSiMeCl_2$	2	$CH_3CH_2CH_2CH(CH_3)CH_2SiMeCl_2$	30

[a] All reactions, except nos. 3 and 6, were at ~30 °C using a 0.05:0.1:5 × 10^{-6} mole ratio of alkene/silane/platinum. Nos. 3 and 6 were run with 0.1:0.05:5 × 10^{-6} mole ratios. Reaction conditions were not optimized, and some of the reactions may have been completed in less time. [b] Yields are based on material isolated by distillation.

hydrosilations offering a potentially useful route to a broad range of important monomers.[3] However, for most cases, the disadvantages of vigorous conditions and highly variable yields,[3] are not compsensated by the recoverability of the catalyst, and thus homogeneous reagents containing platinum, rhodium, or ruthenium have been the reagents of choice for the hydrosilation reaction.[4]

Ultrasonic waves are known to accelerate a variety of reactions, particularly those involving metals.[5,6] We have extended our studies in this area to precious metal catalysis,[7] and in this communication we report on sonically accelerated platinum-on-carbon catalyzed hydrosilations of double and triple bonds. Our results, summarized in Table I, demonstrate that functionalized and nonfunctional silanes can be added across terminal olefins in good yields at ~30 °C, the lowest temperature reported for a Pt/C promoted hydrosilation.



R_3 = Cl_3, Cl_2Me, $(OEt)_3$, Et_3

The influence of sonic waves is such that triethylsilane, a silane that adds to olefins with reluctance (13–30% yields)[3g,h] in the presence of Pt/C even under forcing conditions, gives hexyltriethylsilane in 74% yield when sonicated with 1-hexene and Pt/C for 2 h at room temperature. We also found that triethoxysilane will add very efficiently (93%) to the C=C bond. Phenylacetylene also proved to be an easy substrate for hydrosilation under these conditions, giving 98% isolated yields of the *trans*-(trichlorosilyl)styrene when treated with Cl_3SiH. Similar results were obtained with $MeCl_2SiH$. The more hindered olefin 2-methyl-1-pentene proved more difficult to silate, giving only 71% and 30% yields of adducts with Cl_3SiH and $MeCl_2SiH$, respectively. In the absence of sonic waves no reaction was observed for any of these examples unless the reagents were vigorously agitated for 10–48 h. Yields of adducts were usually below 5%.

In a typical experiment 5.8 g (0.05 mol) of Et_3SiH, 8.4 g (0.1 mol) of 1-hexene, and 0.1 g of 1% Pt/C (5.1 × 10^{-6} mol of Pt) were placed in a 100-mL single-necked flask fitted with a condenser and nitrogen inlet and partly submerged in a common ultrasonic laboratory cleaner (Bransonic Model 220). The bath temperature was maintained at ~30 °C by a 4-in. muffle fan mounted on the side of the cleaner. The flask was positioned at the location in the bath which produced the greatest agitation of the reaction mixture. Often this point was detected by the vigorous bubbling action in the flask and the generation of a misty cloud above the liquid. After 2 h, the vessel was removed from the bath, its contents were filtered, and the filtrate was distilled. The unreacted hexene and triethylsilane were collected by distillation followed by hexyltriethylsilane (7.4 g, 74%; 50 °C (0.02 torr)). The catalyst can be activated prior to the reaction by exposing it to sonic waves. However, the yield of hexyltriethylsilane was only 6%.

Our results show that ultrasonic waves dramatically increase the activity of platinum-on-carbon in the hydrosilation reaction, giving yields of adducts comparable to those obtained with homogeneous catalysts. In each case the reaction proceeded smoothly and without vigorous exotherm. The final product mixture was free of polymer, containing only the unreacted reagents and the desired organosilane. If the products are distilled from the flask without filtration, the catalyst can be recycled many times. Moreover, there appears to be no limitation to scaleup. We are presently investigating the scope and limitations of the

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(1) Presented in part at the 16th Organosilicon Symposium held in conjunction with the 14th Central Region American Chemical Society Meeting, June 16–18, 1982, Midland, MI. Abstract No. 142, Boudjouk, P.; Han, B.-H.; Anfinrud, P.; Anderson, K. R.

(2) Wagner, G. H.; Strother, C. O. U.S. Patent 2632013, 1953.

(3) (a) Wagner, G. H. U.S. Patent 2636738, 1953. (b) Goodman, L.; Silverstein, R. M.; Shoolery, J. N. *J. Am. Chem. Soc.* **1956**, *78*, 4493. (c) Goodman, L.; Silverstein, R. M.; Benitez, A. *Ibid.* **1957**, *79*, 3073–3077. (d) Speier, J. L.; Webster, J. A.; Barnes, G. H. *Ibid.* **1957**, *79*, 974–979. (e) Sommer, L. H.; MacKay, F. P.; Steward, O. W.; Campbell, P. G. *Ibid.* **1957**, *79*, 2764–2769. (f) Benkeser, R. A.; Hickner, R. A. *Ibid.* **1958**, *80*, 5298–5300. (g) Curry, J. W.; Harrison, G. *J. Org. Chem.* **1958**, *23*, 627–628. (h) Topchiev, A. V.; Nametkin, N. S.; Durgar'yan, S. G. *Issled. Obl. Kremniiorg. Soedin.*, **1962**, 28–55; *Chem. Abstr.* **1963**, *59*, 1670.

(4) For a recent review of homogeneous catalysis of hydrosilation see: Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407–447.

(5) (a) Fry, A. J.; Herr, D. *Tetrahedron Lett.* **1978**, *19*, 1721–1724. (b) Luche, J.-L.; Damiano, J. *J. Am. Chem. Soc.* **1980**, *102*, 7926–7927. (c) Han, B.-H.; Boudjouk, P. *Tetrahedron Lett.* **1981**, *22*, 2757–2758. (d) Boudjouk, P.; Han, B.-H. *Ibid.* **1981**, *22*, 3813–3814. (e) Kitazume, T.; Ishikawa, N. *Chem. Lett.* **1981**, 1679–1680. (f) Kitazume, T.; Ishikawa, N. *Ibid.* **1982**, 137–140. (g) Han, B.-H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 751–752. (h) Petrier, C.; Gemal, A. L.; Luche, J.-L. *Tetrahedron Lett.* **1982**, *23*, 3361–3364. (i) Luche, J.-L.; Petrier, C.; Gemal, A. L.; Zikra, N. *J. Org. Chem.* **1982**, *47*, 3805–3806. (j) Repič, O.; Vogt, S. *Tetrahedron Lett.* **1982**, *23*, 2729–2732. (k) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992–4993. (l) Boudjouk, P.; Han, B.-H. *J. Org. Chem.* **1982**, *47*, 5030–5032.

(6) Reactions not involving metals have also been accelerated by sonic waves: (a) Sjoberg, K. *Tetrahedron Lett.* **1966**, 6383–6384. (b) Moon, S.; Duchin, L.; Cooney, J. V. *Ibid.* **1979**, 3917–3920. (c) Lorimer, J. P.; Mason, T. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1136–1137. (d) Kristol, D. S.; Klotz, H.; Parker, R. C. *Tetrahedron Lett.* **1981**, *22*, 907–908. (e) Raucher, S.; Klein, P. *J. Org. Chem.* **1981**, *46*, 3558–3559. (f) Regen, S. L.; Singh, A. *Ibid.* **1982**, *47*, 1587–1588. (g) Han, B.-H.; Boudjouk, P. *Terahedron Lett.* **1982**, *23*, 1643–1646. (h) Boudjouk, P.; Han, B.-H.; Sooriyakumaran, R.; Feil, V., submitted for publication.

(7) (a) Boudjouk, P.; Han, B.-H. "Abstracts of Papers"; 183rd National Meeting of the American Chemical Society, Las Vegas, NV, Mar 1982; American Chemical Society: Washington, DC, 1982; Abstract No. ORGN 190. (b) Boudjouk, P.; Han, B.-H. *J. Catal.* **1983**, *79*, 489–492.

applications of sonic waves to the hydrosilation reaction and to other metal-catalyzed transformations.

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Registry No. $n\text{-}C_6H_{13}SiCl_3$, 928-65-4; $n\text{-}C_6H_{13}SiMeCl_2$, 14799-94-1; $n\text{-}C_6H_{13}SiEt_3$, 13810-04-3; $(CH_3)_2CHCH_2CH_2CH_2SiCl_3$, 20170-36-9; $(CH_3)_2CHCH_2CH_2CH_2SiMeCl_2$, 25959-94-8; $(CH_3)_2CHCH_2CH_2CH_2Si(OEt)_3$, 85356-49-6; $PhCH_2CH_2SiCl_3$, 940-41-0; $PhCH_2CH_2SiMeCl_2$, 772-65-6; $CH_3CH_2CH_2CH(CH_3)CH_2SiCl_3$, 18151-51-4; $CH_3CH_2CH_2CH(CH_3)CH_2SiMeCl_2$, 54008-58-1; $HSiCl_3$, 10025-78-2; $HSiMeCl_2$, 75-54-7; $HSiEt_3$, 617-86-7; $HSi(OEt)_3$, 998-30-1; Pt, 7440-06-4; *trans*-(trichlorosilyl)styrene, 3412-59-7; phenylacetylene, 536-74-3; 1-hexene, 592-41-6; 4-methyl-1-pentene, 691-37-2; styrene, 100-42-5; 2-methyl-1-pentene, 763-29-1.

Reactivity of a Bridged Vinyl Dinuclear Iron Complex Anion, $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]^-$, toward Dicobalt Octacarbonyl: Synthesis of a Mixed Dinuclear Iron Cobalt Bridged Vinyl Complex, $FeCo(CO)_7(\mu\text{-}CHCH_2)$, and Its Thermal Conversion into a Bridged Vinylalkylidene Mixed Trinuclear Cluster, $FeCo_2(CO)_9(\mu_3\text{-}CCH_2)$, and an Ethylidyne Mixed Trinuclear Cluster, $Fe_2Co(CO)_{10}(\mu_3\text{-}CCH_3)$

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Summary: The reaction of $[Fe_2(CO)_7(\mu\text{-}CHCH_2)][P(C_6H_5)_4]$ with $Co_2(CO)_8$ at room temperature results in the formation of $FeCo(CO)_7(\mu\text{-}CHCH_2)$ (**1**) as well as the salt clusters $[Fe(Co_2(CO)_9(\mu_3\text{-}CCH_3)][P(C_6H_5)_4]$ (**2**) and $[Co(CO)_4][P(C_6H_5)_4]$. Heating **1** in refluxing hexane results in redistribution to give the trinuclear clusters $Co_3(CO)_9(\mu_3\text{-}CCH_3)$, $FeCo_2(CO)_9(\mu_3\text{-}CCH_3)$ (**3**), and $Fe_2Co(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CCH_3)$ (**4**).

In a recent study[2] we have shown that $[HFe_3(CO)_{11}]^-$ reacts at room temperature with acetylene to give the μ_3-ethylidyne trinuclear iron complex anion $[Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]^-$ and the μ-vinyl dinuclear iron complex anion $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]^-$. This ease of conversion of acetylene to a μ_3-ethylidyne ligand suggests a facile rearrangement of a μ-vinyl intermediate to a μ_3-ethylidyne ligand on a trinuclear iron unit. For this reason, it was thought that the dinuclear bridged vinyl iron anion might serve as a percursor for a variety of triply bridged ethylidyne mixed-metal clusters by addition of a metal-ligand system. A similar type of study has been developed with a bridged vinylalkylidene complex as a starting material.[3]

Dicobalt octacarbonyl was chosen as the metal-ligand system in the first approach, in the hope that dicobalt octacarbonyl should play a supplementary role, the one of the oxidizing agent, i.e., the reaction shown in eq 1.

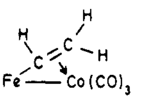

Figure 1. Proposed structure for complex 1.

$$[Fe_2(CO)_7(\mu\text{-}CHCH_2)]^- + Co_2(CO)_8 \rightarrow Fe_2Co(CO)_{10}(\mu_3\text{-}CCH_3) + Co(CO)_4^- + CO \quad (1)$$

Furthermore, cobalt also seemed to favor the transformation of acetylene into the ethylidyne ligand, just as acetylene has been shown to lead to $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ at low temperature with the cluster $HCo_3(CO)_9$.[4] Actually, as is often the case, the reaction is more complex than expected, and even though formation of $Co(CO)_4^-$ has been observed, the reaction does not lead directly to the trinuclear cluster unit.

When stoichiometric amounts of $Co_2(CO)_8$ and $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)][P(C_6H_5)_4]$ are dissolved at room temperature in dichloromethane, a rapid reaction occurs and, after 1 h, no starting material is detected. After solvent evaporation, extraction of the residue with pentane gives a brown solution from which the very volatile brown solid **1** can be isolated with difficulty upon keeping a concentrated pentane solution in dry ice. Both its low melting point and its volatility prevented us from obtaining pure, solvent-free crystals, and it was mainly characterized by infrared, NMR, and mass spectroscopy (Table I). The proton NMR spectrum shows the presence of a vinyl group. In the mass spectrum, a parent ion is detected with a m/z value of 338, while the ions corresponding to the successive loss of seven CO's are observed. The m/z value of 338 agrees with $FeCo(CO)_7CHCH_2$ formula for **1**, and the FeCo ion is detected (m/z 115).

A structure is proposed for **1** with a metal-metal bond between the iron and the cobalt atom. The iron is σ bonded to the vinyl group and to four CO groups, while the cobalt is π bonded to the vinyl group and surrounded by three CO groups (Figure 1). This seems to be the first case of an heterodinuclear complex bridged by a vinyl group.

Upon treatment of the residue of the pentane extraction with diethyl ether, a further complex is dissolved, which can be purified by crystallization from methanol. The infrared spectrum in the CO stretching region (Table I) shows the presence of only terminal CO groups. In the proton NMR spectrum, a complex signal that is characteristic of a $P(C_6H_5)_4$ group and a singlet at 3.65 ppm are observed with an intensity ratio 20/3 that suggests the presence of a CH_3 group in **2**.

Protonation of this anion by trifluoroacetic acid leads to the isolation of the known $CH_3CFeCO_2(CO)_9H$.[5] This result shows **2** to be the $[FeCo_2(CO)_9(\mu_3\text{-}CCH_3)][P(C_6H_5)_4]$ complex. Extraction with ether only leaves $[Co(CO)_4][P(C_6H_5)_4]$ as an insoluble material. The presence of **2** is somewhat surprising and could be the result of the action of $Co(CO)_4^-$ on **1**. Accordingly, we mixed $Co(CO)_4^-$ with **1** and, indeed, **2** is slowly formed at room temperature. Equations 2 and 3 summarize our observations.

$$[Fe_2(CO)_7CHCH_2]^- + Co_2(CO)_8 \rightarrow FeCo(CO)_7CHCH_2 + Co(CO)_4^- + Fe(CO)_4 \quad (2)$$

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[2] Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231.

[3] Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaïen, J.-Y.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 966.

[4] Fachinetti, G.; Puci, S.; Zanazzi, P. F.; Methong, U. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 619.

[5] Eipstein, R. A.; Withers, H. W.; Geoffroy, G. L. *Inorg. Chem.* **1979**, *18*, 942.

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