were also carried out in a similar way. The ^1H NMR spectrum showed that scrambling of deuterium between the methyl and methylene groups of both the $EtPt^A$ and $EtPt^B$ groups was essentially complete. Decomposition of this product gave complex II with significant ^1H content in the bridging hydride position [$\delta(Pt_2H)$ −7.6 ($^1J(PtH)$ = 485 Hz)].

Attempts To Prepare $[Pt_2R_2R^1(\mu\text{-dppm})_2]^+$. Reaction of $[PtPh_2(dppm)]$ with $[PtClMe(dppm)]$ failed to occur, but only slow dimerization of the latter to $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]Cl$ was observed. Reaction of $[PtEt_2(dppm)]$ with $[PtClMe(dppm)]$ gave intractable mixtures, and $[PtMe_2(dppm)]$ with $[PtClEt(dppm)]$ gave $[Pt_2(\mu\text{-}H)Me_2(\mu\text{-dppm})_2]Cl$ as the only isolated product. These reactions are evidently complicated by alkyl transfer leading to scrambling effects.

$[Pt_2Et_2(\mu\text{-}H)(\mu\text{-dppm})_2][SbF_6]$. A solution of $[Pt_2Et_3(\mu\text{-dppm})_2][SbF_6]$ (0.70 g, 0.47 mmol) in CH_2Cl_2 (12 mL) was stored in a closed flask for 70 h in the dark. The color changed from deep orange to dull yellow. The volume of solvent was reduced, and hexane was added to precipitate the product, which was recrystallised from CH_2Cl_2/hexane as an off-white solid: 0.47 g, 69%; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta(^{31}P)$ 14.27 ($^1J(PtP)$ = 3086, $^2J(PtP)$ = 34, $^2J(PP)$ = 51, $^3J(PP)$ = 11 Hz); ^1H NMR (CD_2Cl_2) $\delta(CH_3)$ −0.14 (t, $^3J(HH)$ = 7.8 Hz, $^3J(PtH)$ = 59 Hz), $\delta(CH_2Pt)$ 0.83 (m), $^3J(HH)$ = 7.8 Hz, $^3J(PH)$ = 7.8 Hz), $\delta(CH_2P_2)$ 4.53 (q, $^3J(PtH)$ = 38.5 Hz, $^2J(PH)$ = 3.7 Hz, $^4J(HH)$ = 1.5 Hz), $\delta(PtH)$ −7.65 (m, $^1J(PtH)$ = 488 Hz, $^2J(PH)$ = 9 Hz). Anal. Calcd for $[Pt_2Et_2H(dppm)_2][SbF_6]\cdot 0.1CH_2Cl_2$: C, 44.4; H, 3.8; Cl, 0.5; F, 7.8; P, 8.5. Found: C, 44.4; H, 3.8; Cl, 0.6; F, 7.8; P, 8.5.

Ethylene Analysis. A sample of $[Pt_2Et_3(\mu\text{-dppm})_2][SbF_6]$ (0.050 g, 0.034 mmol) was placed in a small sealable vessel and dissolved in CH_2Cl_2 (1 mL). The vessel was sealed and kept in the dark to prevent photolysis. After 48 h samples of vapor were withdrawn and analyzed by GC. Only ethylene (with no ethane) was detected (82% yield). The solvent was evaporated and the sample redissolved in CH_2Cl_2 (1 mL) as before. After another 48 h a further 1.3% yield of ethylene was obtained, and a third treatment yielded only traces of ethylene and ethane. The GC calibration was made by injecting known volumes of pure ethylene into the above reaction flask containing only CH_2Cl_2 (1 mL) and then, after allowing time for equilibration, sampling as described above. The residue was identified as pure $[Pt_2Et_2(\mu\text{-}H)(\mu\text{-dppm})_2][SbF_6]$ by the ^{31}P NMR spectrum, and the starting material was also shown to contain some of this material by the ^{31}P NMR spectrum. Integration of the complex spectra is inaccurate, but ~10% impurity of IIb in the sample of Ib was detected in this way.

The isotopic analysis was carried out by allowing a solution of Ib and Ic (0.02 g each) in $CHCl_2CHCl_2$ (2 mL) contained in a small vessel fitted with a Teflon tap and quickfit connector to decompose over 48 h at room temperature in the dark. The vessel was cooled in liquid nitrogen, and the volatiles were admitted directly to the mass spectrometer through the gas inlet system. Similar experiments with Ib and Ic separately were carried out, and analysis at 20 and 70 eV was made.

Kinetic Studies. The solution of Ib (0.0029 g in 10 mL of solvent, 2×10^{-4} M solution) was made up in a volumetric flask (10 mL) immediately prior to use and then transferred to a 1-cm cuvette in the thermostated cell compartment of the spectrophotometer. Spectra (370–450 nm) were recorded at suitable intervals. When an additive was required, this was weighed out and mixed with Ib before dissolution. The spectra obtained were identical with those in the absence of added dppm (absorbance by dppm in the range 370–450 nm is very low), indicating that dppm does not interact with either Ib or IIb under the conditions used.

Registry No. Ib, 82311-98-6; Ic, 82312-00-3; IIb, 82312-02-5; III, 52621-09-7; $H[SbF_6]$, 16950-06-4; CD_3CD_2Li, 1629-55-6; CD_3CD_2Br, 3675-63-6; CD_3CH_2Br, 7439-86-3; CH_3CH_2Li, 811-49-4; $PtCl_2(dppm)$, 52595-94-5; $Pt(CD_2CD_3)_2(dppm)$, 82312-03-6; $Pt(CH_2CD_3)_2(dppm)$, 82312-04-7; IV, 82312-05-8; CH_3COCl, 75-36-5; D_2, 7782-39-0.

Reactions of Transition-Metal Nucleophiles with Transition-Metal Electrophiles. Reactions of Acyliron, Acylnickel, and Cobalt Carbonyl Anions with (π-Allyl)palladium Complexes

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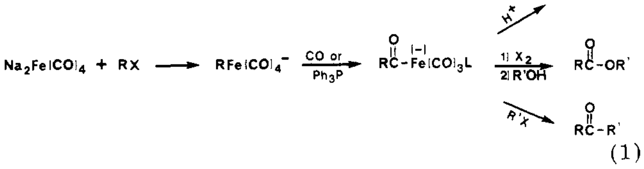
Received June 15, 1982

(π-Allyl)palladium chloride complexes react with anionic acyliron tetracarbonyl complexes and anionic acylnickel carbonyl complexes to produce α,β- and β,γ-unsaturated ketones, resulting from acylation of the π-allyl ligand. A variety of π-allyl complexes and acylmetal complexes were studied. Palladium(II) complexes, including (π-allyl)palladium halides, catalyzed the carbomethoxylation of allyl acetates by $NaCo(CO)_4$. The key step in all of these reactions was thought to be nucleophilic attack of the anionic metal carbonyl complex on a (π-allyl)palladium species.

Introduction

Anionic transition-metal carbonyl complexes have found significant application in organic synthesis because they are at least modest nucleophiles and are quite reactive toward organic electrophiles. A particularly well-studied complex is disodium tetracarbonylferrate, $Na_2Fe(CO)_4$.[1] This strong base (pK_a = 14) and nucleophile reacts in S_N2 fashion with organic halides to produce alkyliron species, which insert carbon monoxide to produce acyl iron species. These can be converted to acylated organic derivatives by further reaction with electrophiles (eq 1).[2,3] A related



(1)

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[1] J. P. Collman, *Acc. Chem. Res.*, 8, 342 (1975).

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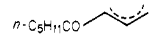
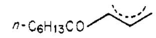
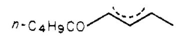
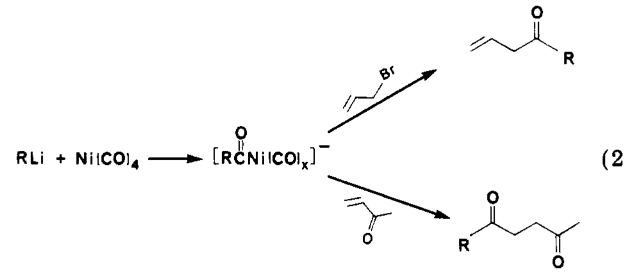
Table I. Acylation of (π-Allyl)palladium Complexes by Acyliron Carbonyl Complexes

Fe complex	Pd complex	products (% yield)[a]
$[n\text{-}C_5H_{11}COFe(CO)_4]^-Na^+$	$[\pi\text{-}C_3H_5PdCl]_2 + 5Ph_3P$	 (51)
	$[\pi\text{-}C_3H_5Pd(diphos)]^+BF_4^-$ [b]	(48)
	$[\pi\text{-}C_3H_5Pd(PPh_3)]^+BF_4^-$	(60)
$[CH_3COFe(CO)_4]^-Li^+$	$[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]^+BF_4^-$	 (53)
$[n\text{-}C_6H_{13}COFe(CO)_3PPh_3]^-Na^+$	$[\pi\text{-}C_3H_5PdCl]_2 + 5Ph_3P + CO$ [c]	 (26)
	$[\pi\text{-}C_3H_5Pd(diphos)]^+BF_4^- + CO$	(27)
$[n\text{-}C_4H_9COFe(CO)_4]^-Li^+$	$[\pi\text{-}1\text{-}MeC_3H_4Pd(PPh_3)]^+BF_4^-$	 (57)[d]

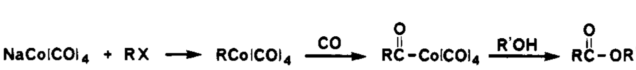
[a] Reported yields for isolated, purified products. [b] diphos = $Ph_2PCH_2CH_2PPh_2$. [c] The reaction was run under an atmosphere of carbon monoxide. [d] A small amount (4%) of the other regioisomer was obtained.

nucleophilic acylmetal complex results from the reaction of nickel carbonyl with organolithium reagents.[3] These unstable acylnickel carbonylates react with allylic halides to produce homoallylic ketones[4] and with conjugated ketones to result in 1,4 acylation (eq 2).[5] The cobalt carbonyl



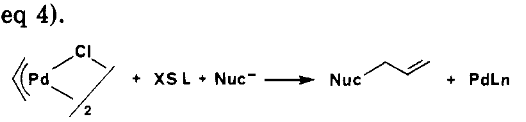
(2)

anion, $Co(CO)_4^-$ ($pK_a = 1$), is considerably less basic than the iron species discussed above but is sufficiently nucleophilic to attack reactive organic halides to form alkyl- and acylcobalt species, convertible to carboxylic acid derivatives (eq 3).[6]



$$NaCo(CO)_4 + RX \longrightarrow RCo(CO)_4 \xrightarrow{CO} R\overset{O}{\overset{\|}{C}}\text{-}Co(CO)_4 \xrightarrow{R'OH} R\overset{O}{\overset{\|}{C}}\text{-}OR' \tag{3}$$

A number of transition-metal organometallic electrophiles are also important in organic synthesis. Foremost among these are the (π-allyl)palladium halide complexes, which react with a variety of nucleophiles, including amines,[7,8] and carbanions[9,10] in the presence of excess ligand (eq 4).

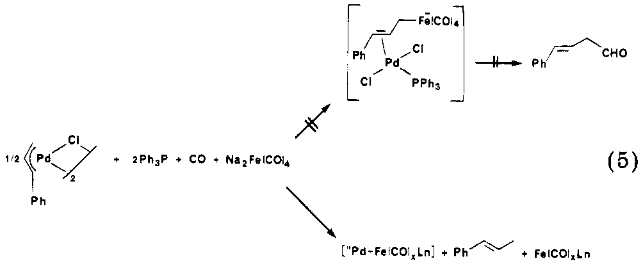


(4)

As part of a general program to explore the reactions of organometallic nucleophiles with organometallic electrophiles, we have studied the reactions of iron, nickel, and cobalt carbonyl anions with (π-allyl)palladium halide complexes. The results of these studies are described herein.

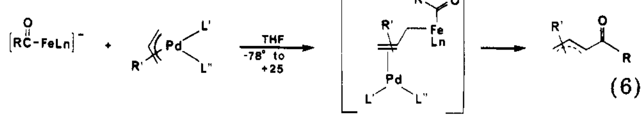
Results and Discussion

Initial studies focused on the reaction of anionic iron carbonyl complexes with (π-allyl)palladium halides. It had previously been reported[11,12] that (π-allyl)palladium chloride reacted with $Fe_2(CO)_9$ to produce the (π-allyl)iron tricarbonyl chloride complex, π-$C_3H_5Fe(CO)_3Cl$, in low yield. Initial attack of iron on the palladium, followed by allyl transfer, was proposed.[13] In the current studies, (π-1-phenylallyl)palladium chloride (1) was treated with disodium tetracarbonylferrate in the presence of triphenylphosphine and carbon monoxide, in an attempt to formylate the π-allyl ligand (eq 5). It was hoped that the



(5)

excess phosphine would divert the iron from palladium to the π-allyl ligand. However, no aldehyde product was obtained. Instead, a gray complex containing palladium in some form[14] and $Fe(CO)_xPPh_3$ (by infrared and NMR spectroscopy) and a yellow mixture of $Fe(CO)_xPPh_3$ and β-methylstyrene (from protonation of the π-allyl group during isolation) were obtained,[15] indicating that the iron anion probably attacked palladium rather than the π-allyl ligand. To circumvent this problem, the considerably less basic acyliron anionic complexes were studied. These complexes converted (π-allyl)palladium complexes to unsaturated ketones in moderate yield (eq 6). The results are summarized in Table I.



(6)

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(2) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Braumann, *J. Am. Chem. Soc.*, **99**, 2515 (1977); **100**, 4766 (1978).

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(5) E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, **91**, 4926 (1969); Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2159 (1968).

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(8) B. M. Trost and J. P. Genet, *J. Am. Chem. Soc.*, **98**, 8516 (1976).

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(10) B. M. Trost, *Tetrahedron*, **33**, 2615 (1977).

(11) C. C. Grindrod, M.Sc. Thesis, McMasters University, Hamilton, Ontario 1966.

(12) A. N. Nesmeyanov, A. Z. Rubezhov, and S. P. Gubin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 194 (1966).

(13) A. N. Nesmeyanov, S. P. Gubin, and A. Z. Rubezhov, *J. Organomet. Chem.*, **16**, 163 (1969).

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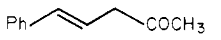
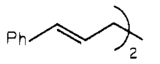
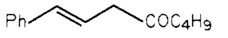
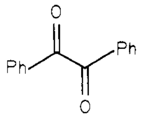
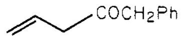
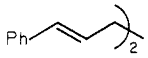
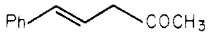
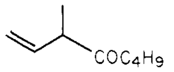
(15) B. C. Benson, W. R. Jackson, K. K. Joshi, and D. T. Thompson, *Chem. Commun.*, 1506 (1968).

Table II. Acylation of (π-Allyl)palladium Complexes by Acylnickel Carbonyl Complexes

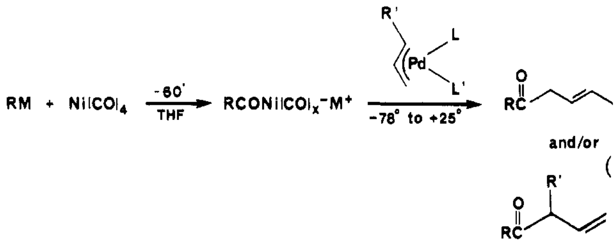
Ni complex	Pd complex	product (% yield)[a]
$CH_3CONi(CO)_xLi$	$[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]^+BF_4^-$	 (61)
		 (15)
$n\text{-}C_4H_9CONi(CO)_xLi$	$[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]^+BF_4^-$	 (45)
$PhCONi(CO)_xLi$	$[\pi\text{-}C_3H_5Pd(PPh_3)]^+BF_4^-$	 (60)
$PhCH_2CONi(CO)_xMgCl$	$[\pi\text{-}C_3H_5Pd(PPh_3)]^+BF_4^-$	 (55)
$CH_3CONi(CO)_xLi$	$[\pi\text{-}1\text{-}PhC_3H_4PdCl]_2$ + $4Ph_3P$	*b*
$CH_3CONi(CO)_xLi$	$[\pi\text{-}1\text{-}PhC_3H_4PdCl]_2$	 (62)
		 (21)
$n\text{-}C_4H_9CONi(CO)_xLi$	$[\pi\text{-}1\text{-}MeC_3H_4Pd(PPh_3)]^+BF_4^-$	 (53)[c]

[a] Reported yields are for isolated purified products. [b] Cinnamyl alcohol was isolated. [c] A small amount (11%) of the other regioisomer was obtained.

The highest yields were obtained in reactions between acyliron tetracarbonyl complexes and cationic mono phosphine (π-allyl)palladium complexes, prepared by the removal of chloride by treatment with silver tetrafluoroborate followed by addition of 1 equiv of triphenylphosphine. This parallels the results obtained in the amination of (π-allyl)palladium complexes, in which cationic monophosphine complexes were most reactive.[16] Complexes resulting from reaction of the chloro-bridged dimer with excess phosphine or with $AgBF_4$ followed by 1,2-bis(diphenylphosphino)ethane (diphos) reacted in somewhat lower yields. The acyliron tetracarbonyl complexes were clearly superior to the corresponding mono(phosphine)iron carbonyl complexes which gave acylation products in only low yield. This result also accounts for the lowering of the yield in reactions involving free triphenylphosphine, since, under these conditions, formation of acyliron carbonyl phosphine complexes certainly occurs. It should be noted that the highest yields of acylation products were obtained with the *least* nucleophilic acyliron species $RCOFe(CO)_4^-$. This stands in contrast to the reaction of organic electrophiles (i.e., alkyl halides) with acyliron complexes, for which the best yields were obtained from the *most* nucleophilic iron species ($Fe(CO)_4^{2-}$ > $RFe(CO)_4^-$ > $RCOFe(CO)_3PPh_3^-$ > $RCOFe(CO)_4^-$).[17] This sensitivity of (π-allyl)palladium complexes to the nucleophilicity of the attacking species is a common feature of this class of compounds[18] and is likely due to the availability of two different sites for nucleophilic attack[19] (the metal and the π-allyl ligand), only one of which (the π-allyl ligand) results in the desired transformation.

Of some importance is the observation that the (π-crotyl)palladium complex also reacted in reasonable yield with acyliron nucleophiles. π-Allyl complexes having protons α to the allyl group often undergo a facile decomposition to the diene by abstraction of one of these protons by base.

Anionic acylnickel carbonyl complexes react with (π-allyl)palladium complexes in a similar fashion (eq 7; Table II).



(7)

Since these nickel complexes are both less reactive and less thermally stable than the corresponding iron complexes, only the most reactive (π-allyl)palladium complexes, the cationic, monophosphine complexes, underwent acylation. In contrast to the iron case, only the β,γ-unsaturated ketone was obtained, the acylnickel complex being less basic than the corresponding iron species and thus being unable to effect rearrangement.

The chloro-bridged dimer was inert in the presence of excess triphenylphosphine, the allyl group being recovered as the corresponding allylic alcohol after the oxidative (I_2) isolation procedure. In the absence of triphenylphosphine, reduction of the chlorobridged dimer was observed. Palladium metal was deposited from solution, and the major product was the biallyl from reductive coupling of the π-allyl groups. In this case, it is likely that the anionic nickel complex attack palladium directly rather than attack the π-allyl group. Only a low yield of the acylation product was obtained. The acylnickel complexes from methyllithium, n-butyllithium, and benzylmagnesium chloride acylated (π-allyl)palladium complexes in fair yield. In contrast, that from phenyllithium was unreactive under conditions sufficiently severe to cause thermal decomposition to benzil ($\simeq$25 °C), and no acylation resulted from this reactant. The (π-crotyl)palladium complex reacted with the acylnickel species from n-butyllithium to give good yields of acylation product. Again, the possible base-promoted decomposition of the π-allyl complex to butadiene was not observed. Surprisingly, acylation occurred at the more substituted terminus of this complex.

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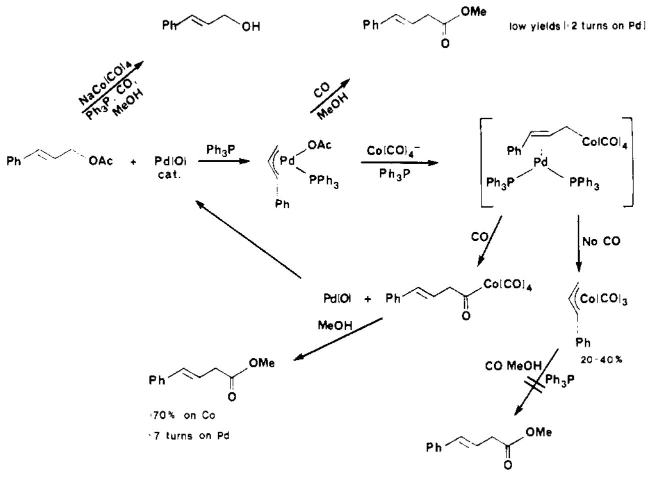
(16) B. Åkermark, G. Åkermark, L. S. Hegedus, and K. Zetterberg, *J. Am. Chem. Soc.*, **103**, 3037 (1981).

(17) J. P. Collman, S. R. Winter, and D. R. Clark, *J. Am. Chem. Soc.*, **94**, 1788 (1972).

(18) a) B. M. Trost, L. Weber, P. A. Strege, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, **100**, 3416, 3426 (1978); b) B. M. Trost and T. R. Verhoeven, *ibid.*, **102**, 4730 (1980); c) L. S. Hegedus, W. H. Darlington, and C. E. Russell, *J. Org. Chem.*, **45**, 5193 (1980).

(19) S.-i. Murahashi, Y. Tamba, M. Yamamura, and N. Yoshimura, *J. Org. Chem.*, **43**, 4099 (1978).

Scheme I



The final metal carbonyl anion studied was sodium tetracarbonylcobaltate, $NaCo(CO)_4$. In contrast to the nickel and iron complexes discussed above, this species does not contain an acyl group (RCO) and should function as a CO-transfer agent rather than an acyl-transfer agent. Scheme I describes a palladium(0) catalyzed carboalkoxylation of allyl acetates by sodium tetracarbonylcobaltate in the presence of triphenylphosphine and carbon monoxide, in which a key step is thought to be nucleophilic attack of the cobalt anion on a (π-allyl)palladium species (Scheme I).

Several features indicate that this process is indeed bimetallic. Reaction of cinnamyl acetate with $NaCo(CO)_4$ alone led to simple hydrolysis of this ester, producing cinnamyl alcohol and no methyl ester. Thus, the cobalt anion is too weak a nucleophile to attack an allylic acetate and produce a (σ-allyl)- or (π-allyl)cobalt complex. Addition of a palladium catalyst (either 10% $PdCl_2(CH_3CN)_2/6Ph_3P$ or 5% $[\pi\text{-1-PhC}_3H_4PdCl]_2/8Ph_3P$) resulted in carbomethoxylation of the allylic acetate in over 70% yield, based on cobalt. This corresponds to about seven cycles of the palladium catalyst. The reaction is thought to occur by formation of a (π-allyl)palladium complex by an oxidative addition of the allyl acetate to a palladium(0) species followed by nucleophilic attack of the cobalt anion on this π-allyl species. (π-Allyl)palladium complexes themselves are known to carbonylate when treated with carbon monoxide and methanol.[20] However, under the conditions used in Scheme I, only low yields of ester (less than two turns of the palladium catalyst) were obtained in the absence of the cobalt anion. Under a carbon monoxide atmosphere, the (σ-allyl)cobalt species resulting from attack of the cobalt anion on the (π-allyl)palladium species inserted carbon monoxide to give a (σ-acyl)cobalt species, which methanol cleaved to produce the desired ester in over 70% yield, based on cobalt (~ seven cycles of the palladium catalyst). When the reaction was carried out in the *absence* of carbon monoxide, the corresponding (π-allyl)cobalt was isolated in 20–40% yield (two to four cycles of the palladium). This strongly indicates that palladium is activating the allyl acetate via a (π-allyl)palladium complex and that the π-allyl group is transferred to cobalt.[21] In the absence of carbon monoxide, the initially formed (σ-allyl)cobalt complex collapses to a π-allyl complex. It has already been shown that these (π-allyl)cobalt complexes do not form the desired ester when exposed to CO and methanol[22] and that isomerization back to the σ-allyl complex is a difficult process.[23] Thus, CO insertion in the initially formed σ-allyl complex in Scheme I is proposed.

Experimental Section

General Data. Melting points were taken with a Mel-Temp apparatus and are uncorrected. Infrared spectra were determined on a Beckman Model 4200 spectrophotometer and are reported in inverse centimeters. Nuclear magnetic resonance (NMR) spectra were measured with either a Varian Associates Model T-60 or EM-360 or JEOL FX-100 spectrophotometer using Me_4Si as the internal standard and are reported in δ. Coupling constants are given in hertz. Mass spectra were taken on a VG Micromass 16F mass spectrometer at an ionization energy of 70 eV. Analytical thin-layer chromatography was performed by using Brinkman precoated silica gel F-254 plates (0.25 mm). Preparative thin-layer chromatography was performed by using 20 × 20 cm plates coated with silica gel (2 mm, E M Laboratories 60 PF-254). Products were visualized with UV light. Purity of products was established by comparison of NMR spectra, thin-layer chromatography, and vapor-phase chromatography comparison with authentic material. All products were >95% pure by these criteria.

Materials. All solvents were freshly distilled and stored under an argon atmosphere. Immediately before use they were degassed and saturated with argon. Tetrahydrofuran (THF) and ether were distilled from sodium benzophenone ketyl. Disodium tetracarbonylferrate–dioxane (3/2) $[Na_2Fe(CO)_4{\cdot}1.5(C_4H_8O_2)]$ (Alfa), pentacarbonyliron $[Fe(CO)_5]$ (Alfa), and nickel carbonyl $[Ni(CO)_4]$ (Pressure Chemical Co.) were used without further purification. Octacarbonyldicobalt $[Co_2(CO)_8]$ (Alfa) was recrystallized from petroleum ether. Hexanoyl chloride (Matheson Coleman and Bell) and *n*-hexyl bromide (Aldrich) were used without further purification. Methyllithium, *n*-butyllithium, and benzylmagnesium chloride, purchased from Aldrich as a 1.6 M ether solution, Alfa as a 2.4 M hexane solution, and Alfa as a 1.1 M THF solution, respectively, were titrated by using the 2-butanol–1,10-phenanthroline method of Watson and Eastham.[24] Phenyllithium was prepared in ether by a published procedure[25] and titrated by using the above method. Triphenylphosphine (Aldrich) and silver tetrafluoroborate (Alfa) were used without further purification.

The complex $[(n\text{-}C_5H_{11})COFe(CO)_4]Na$ was prepared from $Na_2Fe(CO)_4$ and $n\text{-}C_5H_{11}COCl$ in THF by a published procedure[26] and used as a THF solution.

The complexes $[CH_3COFe(CO)_4]Li$ and $[n\text{-}C_4H_9COFe(CO)_4]Li$ were prepared from $Fe(CO)_5$ and the corresponding alkyllithium in THF by a published procedure[27] and used as a THF solution. The complex $[n\text{-}C_6H_{13}COFe(CO)_3PPh_3]Na$ was prepared from $Na_2Fe(CO)_4$, $n\text{-}C_6H_{13}Br$, and PPh_3 in THF by a published procedure.[28] The complexes $[CH_3CONi(CO)_x]Li$, $[n\text{-}C_4H_9CONi(CO)_x]Li$, and $[PhCONi(CO)_x]Li$ were prepared from $Ni(CO)_4$ and the corresponding alkyl- or aryllithium in ether by a published procedure[3,5] and used as an ether solution.

The complex $[PhCH_2CONi(CO)_x]MgCl$ was prepared in THF. $Ni(CO)_4$ (0.20 mL, 1.5 mmol) was added to 5 mL of argon saturated THF. The solution was cooled to −50 °C, and benzylmagnesium chloride (1.5 mL of 1.01 M in THF) was added. The mixture was stirred for 3.5 h at −50 °C and used for further reaction.

The compound $NaCo(CO)_4$ was prepared from octacarbonyldicobalt and NaH in THF by a published procedure[29] and used

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as a THF solution. (π-Allyl)palladium chloride, (π-1-methylallyl)palladium chloride, and (π-1-phenylallyl)palladium chloride were prepared from $PdCl_2(CH_3CN)_2$ and the corresponding allylic chloride compounds by a published procedure.[30] 1,2-Bis(diphenylphosphino)ethane (diphos) was prepared by a published procedure.[31] Cationic π-allylic palladium complexes such as $[\pi\text{-}C_3H_5Pd(diphos)]BF_4$, $[\pi\text{-}C_3H_5Pd(PPh_3)]BF_4$, $[\pi\text{-}1\text{-}MeC_3H_4Pd(PPh_3)]BF_4$, and $[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]BF_4$ were prepared by a published procedure.[16]

Attempted Formylation of $[\pi\text{-}1\text{-}PhC_3H_4PdCl]_2$ with $Na_2Fe(CO)_4$ in the Presence of Excess Triphenylphosphine. A solution of $[\pi\text{-}1\text{-}PhC_3H_4PdCl]_2$ (0.13 g, 0.30 mmol) and triphenylphosphine (0.32 g, 1.2 mmol) in THF (8 mL) (precooled to −78 °C) was added to $Na_2Fe(CO)_4\cdot1.5(C_4H_8O_2)$ (0.21 g, 0.60 mmol) in THF (10 mL) over 5 min via a precooled (dry ice) syringe at −78 °C under a carbon monoxide atmosphere. The reaction solution was slowly allowed to warm to room temperature and stirred for an additional 3 h.

Glacial acetic acid (0.069 mL, 1.2 mmol) was added and the mixture stirred for 10 min. The mixture was poured into water (100 mL) and extracted with ether (3 × 30 mL). The combined extracts were washed with water (3 × 20 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent was concentrated on a rotary evaporator. The residue was treated with a small portion of pentane and filtered. A dark gray solid (0.19 g) was obtained: IR (KBr) 2038, 1968, 1925, cm^{-1}; NMR ($CDCl_3$) δ 7.33 (s, 2), 7.77 (s, 3). Palladium was detected by using dimethylglyoxime.[14]

The filtrate was concentrated to give a mixture (0.14 g) of yellow solid and a small amount of liquid: IR (Nujol) 2038, 1968, 1925, cm^{-1}. The liquid was *trans*-propenylbenzene, identical with authentic material (Columbia Organic Chemicals Co.).

General Reaction Procedure for Acylation of (π-Allyl)palladium Chloride with Acyliron Carbonyl Complexes in the Presence of Excess Triphenylphosphine. To a solution of $[\pi\text{-}C_3H_5PdCl]_2$ and triphenylphosphine in THF cooled to −60 °C under an argon atmosphere was added a THF solution of $[n\text{-}C_5H_{11}COFe(CO)_4]Na$ (precooled to −78 °C) over 5 min via a precooled (dry ice) syringe. The initial dark brown mixture turned into a yellow suspension within 10 min. After the reaction mixture was stirred for an additional 45 min at −60 °C, it was slowly allowed to warm to room temperature. The mixture was diluted with ether (100 mL) and cooled to −78 °C, followed by filtration to give a yellow solid. This solid was tetrakis(triphenylphosphine)palladium(0), $[Pd(PPh_3)_4]$, and all spectral data coincided with those of the authentic sample.[32] The filtrate was washed with water (3 × 30 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent was concentrated on a rotary evaporator. The residue was treated with a small portion of pentane, and the insoluble compounds were removed by filtration. The crude product was obtained after evaporation of the solvent.

With $[n\text{-}C_5H_{11}COFe(CO)_4]Na$. A solution of $[n\text{-}C_5H_{11}COFe(CO)_4]Na$ (1.8 mmol) in THF (10 mL) was added to a solution of $[\pi\text{-}C_3H_5PdCl]_2$ (0.31 g, 0.85 mmol) and triphenylphosphine (2.2 g, 8.5 mmol) in THF (10 mL). $Pd(PPh_3)_4$ (1.1 g, 56%) was obtained. Purification by evaporative distillation (95–105 °C (11 torr)) gave 0.12 g (50%) of 2-nonen-4-one, in all respects identical with material prepared by an alternate procedure.[33]

With $[n\text{-}C_6H_{13}COFe(CO)_3PPh_3]Na$. A solution of $[n\text{-}C_6H_{13}COFe(CO)_3PPh_3]Na$ (1.6 mmol) in THF (9 mL) was added to a solution of $[\pi\text{-}C_3H_5PdCl]_2$ (0.28 g, 0.76 mmol) and triphenylphosphine (2.0 g, 7.6 mmol) in THF (10 mL). The reaction was run under a carbon monoxide atmosphere. $Pd(PPh_3)_4$ (1.3 g, 75%) was obtained. Purification by evaporative distillation (100–110 °C (11 torr)) gave 0.060 g (26%) of the 90:10 mixture of 2-decen-4-one and 1-decen-4-one, in all identical respects with materials prepared by alternate procedures.[33]

General Reaction Procedure for Acylation of Cationic π-Allylic Palladium Complexes with Acyliron Carbonyl Complexes. A THF solution of the acyliron carbonyl complex (precooled at −78 °C) was added to a THF solution of the cationic π-allylic palladium complex cooled to −78 °C over 5 min via a precooled (dry ice) syringe under an argon atmosphere. After the reaction mixture was slowly allowed to warm to room temperature, ether (100 mL) was added, and the mixture was filtered. The filtrate was washed with water (3 × 30 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent was concentrated on a rotary evaporator. The residue was treated with a small portion of pentane, and the insoluble compounds were removed by filtration. The crude product was obtained after evaporation of the solvent.

Reaction of $[\pi\text{-}C_3H_5Pd(diphos)]BF_4$ with $[n\text{-}C_5H_{11}COFe(CO)_4]Na$. A solution of $[n\text{-}C_5H_{11}COFe(CO)_4]Na$ (1.05 mmol) in THF (7 mL) was added to a solution of $[\pi\text{-}C_3H_5Pd(diphos)]BF_4$ (1.0 mmol) in THF (20 mL). Purification by evaporative distillation (95–105 °C (11 torr)) gave 0.067 g (48%) of the 15:85 mixture of 2-nonen-4-one and 1-nonen-4-one, in all respects identical with materials prepared by alternate procedures.[33]

Reaction of $[\pi\text{-}C_3H_5Pd(PPh_3)]BF_4$ with $[n\text{-}C_5H_{11}COFe(CO)_4]Na$. A solution of $[n\text{-}C_5H_{11}COFe(CO)_4]Na$ (0.85 mmol) in THF (5 mL) was added to a solution of $[\pi\text{-}C_3H_5Pd(PPh_3)]BF_4$ (0.81 mmol) in THF (15 mL). Purification by evaporative distillation (140–150 °C (19 torr)) gave 0.068 g (60%) of the 45:55 mixture of 2-nonen-4-one and 1-nonen-4-one.

Reaction of $[\pi\text{-}C_3H_5Pd(diphos)]BF_4$ with $[n\text{-}C_6H_{13}COFe(CO)_3PPh_3]Na$. A solution of $[n\text{-}C_6H_{13}COFe(CO)_3PPh_3]Na$ (1.3 mmol) in THF (9 mL) was added to a solution of $[\pi\text{-}C_3H_5Pd(diphos)]BF_4$ (1.2 mmol) in THF (25 mL). The reaction was run under a carbon monoxide atmosphere. Purification by evaporative distillation (100–110 °C (11 torr)) gave 0.052 g (27%) of 53:47 mixture of 2-decen-4-one and 1-decen-4-one.

Reaction of $[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]BF_4$ with $[CH_3COFe(CO)_4]Li$. A solution of $[CH_3COFe(CO)_4Li$ (1.2 mmol) in THF (8 mL) was added to a solution of $[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]BF_4$ (1.0 mmol) in THF (30 mL). Purification by preparative layer chromatography (silica gel, 2:1 hexane–ether, R_f 0.40) gave 0.085 g (53%) of the 83:17 mixture of methyl *trans*-cinnamyl ketone and 5-phenyl-3-penten-2-one, in all respects identical with materials prepared by alternate procedures.[5,34]

Reaction of $[\pi\text{-}1\text{-}MeC_3H_4Pd(PPh_3)]BF_4$ with $[n\text{-}C_4H_9COFe(CO)_4]Li$. A solution of $[n\text{-}C_4H_9COFe(CO)_4]Li$ (1.2 mmol) in THF (5 mL) was added to a solution of $[\pi\text{-}1\text{-}MeC_3H_4Pd(PPh_3)]BF_4$ (1.0 mmol) in THF (20 mL). Purification by evaporative distillation (80–90 °C (6 torr)) gave 0.086 g (61%) of the 68:28:4 mixture of 2-nonen-5-one, 3-nonen-5-one, and 3-methyl-1-octen-4-one, respectively. 3-Nonen-5-one was in all respects identical with material prepared by an alternate procedure.[35] 2-Nonen-5-one: NMR ($CDCl_3$) δ 5.60–5.45 (m, 2, HC═CH), 3.13–3.04 (m, 2, ═CCH$_2$C═O), 2.40 (t, J = 7.4 Hz, 2, CH$_2$C═O), 1.68 (d, J = 3.5 Hz, 3, CH$_3$C═), 1.65–1.47 (tt, J = 7.1, 7.4 Hz, 2, CH$_2$CC═O), 1.40–1.22 (tq, J = 7.1, 7.6 Hz, 2, CH$_2$CCC═O), 0.88 (t, J = 7.6 Hz, 3, CH$_3$C); IR (neat) 1708 (C═O), 1660, 960 (trans, CH═CH) cm^{-1}; mass spectrum, m/e (relative intensity) 140.0 (parent, 5.6), 111.0 (2.7), 98.0 (6.4), 85.1 (100), 83.1 (3.0).

3-Methyl-1-octen-4-one:[36] NMR ($CDCl_3$) δ 5.79 (ddd, J = 17.5, 10.7, 8.9 Hz, 1, ═CHC), 5.14 (dd, J(trans) = 17.5 Hz, 1, HC═CC), 5.12 (dd, J(cis) = 10.7 Hz, 1, HC═CC), 3.19 (dq, J = 7.3, 8.9 Hz, 1, ═CCHC═O), 2.41 (t, J = 7.8 Hz, 2, CH$_2$C═O), 1.65–1.47 (tt, J = 7.8, 7.6 Hz, 2, CH$_2$CC═O), 1.42–1.23 (tq, J = 7.6, 7.6 Hz, 2, CH$_2$CCC═O), 1.16 (d, J = 7.3 Hz, 3, CH$_3$CC═), 0.90 (t, J = 7.6 Hz, 3, CH$_3$C); IR (neat) 1707 (C═O), 988, 911 (═CH$_2$) cm^{-1}; mass spectrum, m/e (relative intensity) 140.0 (parent, 3.1), 125.2 (6.9), 98.1 (9.3), 85.1 (100), 83.1 (40.5).

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General Reaction Procedure for Acylation of π-Allylic Palladium Complexes with Acylnickel Carbonyl Complexes. *Caution*!! Nickel carbonyl is an exceedingly toxic, volatile (bp 43 °C) complex. All operations involving this compound must be carried out in an efficient draft hood.[5] A THF solution of the π-allylic palladium complex (precooled to −78 °C) was added to a solution of the acylnickel carbonyl complex in ether or THF cooled to −78 °C, over 5 min via a precooled (dry ice) syringe under an argon atmosphere. The reaction mixture was slowly allowed to warm to room temperature and then stirred for an additional 1 h. Aqueous ammonium chloride solution (10 mL) was added, and excess nickel carbonyl was decomposed by the addition of iodine in ether until the evolution of carbon monoxide ceased and the solution remained brown from excess I_2 for 1 h. The mixture was poured into a separatory funnel containing ether (100 mL) and water (50 mL) and was shaken. The ether layer was washed with aqueous sodium bisulfite solution (50 mL) to decompose excess iodine and water (2 × 50 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent was concentrated on a rotary evaporator. When triphenylphosphine was contained in the π-allylic palladium complex, the residue was treated with a small portion of pentane and the insoluble triphenylphosphine oxide was removed by filtration. The crude product was obtained after evaporation of the solvent.

Reaction of $[\pi\text{-1-PhC}_3\text{H}_4\text{Pd(PPh}_3)]\text{BF}_4$ with $[\text{CH}_3\text{CONi(CO)}_x]\text{Li}$. A solution of $[\pi\text{-1-PhC}_3\text{H}_4\text{Pd(PPh}_3)]\text{BF}_4$ (1.0 mmol) in THF (30 mL) was added to a solution of $[\text{CH}_3\text{CONi(CO)}_x]\text{Li}$ (1.5 mmol) in ether (5 mL). Purification by preparative layer chromatography (silica gel, 2:1 hexane–ether) gave 0.098 g (61%) of methyl *trans*-cinnamyl ketone (R_f 0.40) and 0.018 g (15%) of 1,6-diphenyl-1,5-hexadiene (R_f 0.90). These materials were in all respects identical with materials prepared by alternate procedures, respectively.[5,35]

Reaction of $[\pi\text{-1-PhC}_3\text{H}_4\text{Pd(PPh}_3)]\text{BF}_4$ with $[n\text{-C}_4\text{H}_9\text{CONi(CO)}_x]\text{Li}$. A solution of $[\pi\text{-1-PhC}_3\text{H}_4\text{Pd(PPh}_3)]\text{BF}_4$ (1.0 mmol) in THF (30 mL) was added to a solution of $[n\text{-C}_4\text{H}_9\text{CONi(CO)}_x]\text{Li}$ (1.5 mmol) in ether (5 mL). Purification by preparative layer chromatography (silica gel, 2:1 hexane–ether, R_f 0.70) gave 0.091 g (45%) of *n*-butyl *trans*-cinnamyl ketone, in all respects identical with material prepared by an alternative procedure.[5]

Reaction of $[\pi\text{-C}_3\text{H}_5\text{Pd(PPh}_3)]\text{BF}_4$ with $[\text{PhCONi(CO)}_x]\text{Li}$. A solution of $[\pi\text{-C}_3\text{H}_5\text{Pd(PPh}_3)]\text{BF}_4$ (1.0 mmol) in THF (15 mL) was added to a solution of $[\text{PhCONi(CO)}_x]\text{Li}$ (1.5 mmol) in ether (5 mL). Crude product (0.18 g) was benzil, in all respects identical with authentic material: NMR Sadtler No. 73; IR Sadtler No. 922.

Reaction of $[\pi\text{-C}_3\text{H}_5\text{Pd(PPh}_3)]\text{BF}_4$ with $[\text{PhCH}_2\text{CONi(CO)}_x\text{MgCl}]$. A solution of $[\pi\text{-C}_3\text{H}_5\text{Pd(PPh}_3)]\text{BF}_4$ (1.0 mmol) in THF (15 mL) was added to a solution of $[\text{PhCH}_2\text{CONi(CO)}_x MgCl]$ (1.5 mmol) in THF (5 mL). Purification by preparative layer chromatography (silica gel, 2:1 hexane–ether, R_f 0.60) gave 0.088 g (55%) of benzyl allyl ketone: NMR (CDCl_3) 3.19 (d, J = 7 Hz, 2, $\text{C{=}CCH}_2\text{C{=}O}$), 3.70 (s, 2), 4.83–5.33 (m, 1), 5.46–6.29 (m, 1), 6.97–7.57 (m, 5); IR (neat) 1705 (C=O), 1627, 984, 913 ($\text{CH{=}CH}_2$) cm^{-1}; mass spectrum, m/e (relative intensity) 160.1 (parent, 6.4), 119.0 (13.5), 99.0 (7.5), 91.0 (100), 69.0 (20.3), 65.1 (13.2).

Reaction of $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ with $[\text{CH}_3\text{CONi(CO)}_x]\text{Li}$ in the Presence of Excess Triphenylphosphine. A solution of $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ (0.22 g, 0.5 mmol) and triphenylphosphine (1.1 g, 4.0 mmol) in THF (15 mL) was added to a solution of $[\text{CH}_3\text{CONi(CO)}_x]\text{Li}$ (1.5 mmol) in ether (5 mL). Purification by preparative layer chromatography (silica gel, 1:1 hexane–ether, R_f 0.30) gave 0.037 g (28%) of cinnamyl alcohol identical with authentic material: NMR Sadtler No. 23; IR Sadtler No. 184.

Reaction of $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ with $[\text{CH}_3\text{CONi(CO)}_x]\text{Li}$. A solution of $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ (0.26 g, 0.5 mmol) in THF (25 mL) was added to a solution of $[\text{CH}_3\text{CONi(CO)}_x]\text{Li}$ (1.5 mmol) in ether (5 mL). Purification by preparative layer chromatography (silica gel, 2:1 hexane–ether) gave 0.034 g (21%) of methyl *trans*-cinnamyl ketone (R_f 0.40) and 0.073 g (62%) of 1,6-diphenyl-1,5-hexadiene (R_f 0.09).

Reaction of $[\pi\text{-1-MeC}_3\text{H}_4\text{Pd(PPh}_3)]\text{BF}_4$ with $[n\text{-C}_4\text{H}_9\text{CONi(CO)}_x]\text{Li}$. A solution of $[\pi\text{-1-MeC}_3\text{H}_4\text{Pd(PPh}_3)]\text{BF}_4$ (1.0 mmol) in THF (20 mL) was added to a solution of $[n\text{-C}_4\text{H}_9\text{CONi(CO)}_x]\text{Li}$ (1.5 mmol) in ether (5 mL). Purification by evaporative distillation (80–90 °C (6 torr)) gave 0.098 g (70%) of the 16:9:75 mixture of 2-nonen-5-one, 3-nonen-5-one, and 3-methyl-1-octen-4-one, respectively. These materials were identical with those prepared above by using acyliron chemistry.

General Procedure for Carbomethoxylation of Cinnamyl Acetate with NaCo(CO)_4 in the Presence of Palladium Catalyst. To a solution of cinnamyl acetate, palladium catalyst, and triphenylphosphine in THF cooled to −60 °C was added to a THF solution of NaCo(CO)_4 (precooled to −78 °C) over 5 min via a precooled (dry ice) syringe under a carbon monoxide atmosphere. The reaction mixture was slowly allowed to warm to room temperature. The initial colorless solution gradually turned amber above −50 °C. Methanol and diisopropylethylamine were added at room temperature, and the mixture was stirred overnight. After filtration, ether (100 mL) was added to the filtrate. The ether solution was washed with aqueous 2 N HCl solution (30 mL) and water (3 × 30 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent concentrated on a rotary evaporator.

Reaction Using $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ as a Catalyst. A mixture of cinnamyl acetate (2.3 g, 13 mmol), $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.26 g, 1.0 mmol), and triphenylphosphine (1.6 g, 6.0 mmol) in THF (20 mL) was stirred for 48 h at room temperature under a carbon monoxide atmosphere to prepare the active catalyst, and then a solution of NaCo(CO)_4 (9.2 mmol) in THF (40 mL) was added to this mixture at −60 °C. Methanol (20 mL) and diisopropylethylamine (2.4 mL) were added. Purification by reduced pressure distillation (90 °C (0.5 torr)) gave 1.2 g (650% based on Pd, 70% based on cobalt) of methyl 4-phenyl-3-butenoate, in all respects identical with material prepared by an alternate procedure.[36]

Reaction Using $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ as a Catalyst. A mixture of cinnamyl acetate (0.42 g, 2.4 mmol), $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ (0.053 g, 0.12 mmol), and triphenylphosphine (0.25 g, 0.95 mmol) in THF (10 mL) was stirred for 5 min at room temperature under a carbon monoxide atmosphere, and then a solution of NaCo(CO)_4 (1.9 mmol) in THF (15 mL) was added to this mixture at −60 °C. Methanol (10 mL) and diisopropylethylamine (0.49 mL) were added. Purification by evaporative distillation (100–110 °C (0.5 torr)) gave 0.24 g of 88:12 mixture of methyl 4-phenyl-2-butenoate (510% based on Pd, 64% based on cobalt) and cinnamyl acetate.

Reaction without Palladium Catalyst. A solution of NaCo(CO)_4 (1.4 mmol) in THF (15 mL) was added to a solution of cinnamyl acetate (0.22 g, 1.3 mmol) and triphenylphosphine (0.16 g, 0.63 mmol) in THF (10 mL) at −60 °C under a carbon monoxide atmosphere. Methanol (5 mL) and diisopropylethylamine (0.24 mL) were added. Purification by preparative layer chromatography (silica gel, 1:1 hexane–ether, R_f 0.30) gave 0.13 g (80%) of cinnamyl alcohol.

Reaction Using $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ as a Catalyst without NaCo(CO)_4. A mixture of cinnamyl acetate (0.18 g, 1 mmol), $[\pi\text{-1-PhC}_3\text{H}_4\text{PdCl}]_2$ (0.022 g, 0.05 mmol), and triphenylphosphine (0.11 g, 0.42 mmol) in THF (10 mL) was stirred overnight at room temperature under a carbon monoxide atmosphere. Methanol (5 mL) and diisopropylethylamine (0.17 mL) were added. Purification by evaporative distillation (100–110 °C (0.5 torr)) gave 0.10 g of 37:63 mixture of methyl 4-phenyl-3-butenoate (210% based on Pd) and cinnamyl acetate.

Formation of $[\pi\text{-C}_3\text{H}_5\text{Co(CO)}_2\text{PPh}_3]$. To a solution of allyl acetate (0.19 mL, 1.8 mmol), $[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2$ (0.032 g, 0.088 mmol), and triphenylphosphine (0.092 g, 0.35 mmol) in THF (20 mL) cooled to −60 °C was added a solution of NaCo(CO)_4 (1.9 mmol) in THF (20 mL) (precooled to −78 °C) over 5 min under an argon atmosphere. The reaction mixture was allowed to slowly warm to room temperature and then stirred for an additional 3 h. A solution of PPh_3 (0.46 g, 1.8 mmol) in THF (5 mL) was added, and the reaction mixture was stirred overnight. The mixture was centrifuged, and the supernatant was evaporated to dryness. The residue was treated with a small portion of pentane, and the insoluble compounds were removed by filtration. The filtrate was concentrated to dryness to give 0.016 g (22%) of an orange solid, $[\pi\text{-C}_3\text{H}_5\text{Co(CO)}_2\text{PPh}_3]$ (mp 110 °C dec), whose infrared spectrum was identical with that of the authentic material.[22]

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Registry No. 1, 12131-44-1; disodium tetracarbonylferrate, 14878-31-0; PPh_3, 603-35-0; $PhCH{=}CHCH_3$, 637-50-3; $[n\text{-}C_5H_{11}COFe(CO)_4]^-Na^+$, 82456-27-7; $[CH_3COFe(CO)_4]^-Li^+$, 71722-65-1; $[n\text{-}C_6H_{13}COFe(CO)_3PPh_3]^-Na^+$, 82456-28-8; $[n\text{-}C_4H_9COFe(CO)_4]^-Li^+$, 31627-07-3; $[\pi\text{-}C_3H_5PdCl]_2$, 12012-95-2; $[\pi\text{-}C_3H_5Pd(diphos)]^+Bf_4^-$, 82456-29-9; $[\pi\text{-}C_3H_5Pd(PPh_3)]^+BF_4^-$, 82456-31-3; $[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]^+BF_4^-$, 82456-33-5; CO, 630-08-0; $[\pi\text{-}1\text{-}MeC_3H_4Pd(PPh_3)]^+BF_4^-$, 58527-38-1; $n\text{-}C_5H_{11}COCH{=}CHCH_3$, 32064-72-5; (*E*)-$PhCH{=}CHCH_2COCH_3$, 42762-56-1; $n\text{-}C_6H_{13}COCH{=}CHCH_3$, 63024-86-2; $n\text{-}C_4H_9COCH{=}CHCH_2CH_3$, 82456-34-6; $n\text{-}C_5H_{11}COCH_2CH{=}CH_2$, 61168-10-3; $PhCH_2CH{=}CHCOCH_3$, 10521-97-8; $n\text{-}C_6H_{13}COCH_2CH{=}CH_2$, 65807-57-0; $n\text{-}C_4H_9COCH_2CH{=}CH\text{-}CH_3$, 82456-35-7; $PhCH{=}CHCH_2CH_2CH{=}CHPh$, 4439-45-6; $PhCH{=}CHCH_2COC_4H_9$, 82456-36-8; PhCOCOPh, 134-81-6; $H_2C{=}CH\text{-}CH_2COCH_2Ph$, 82456-37-9; $PhCH{=}CHCH_2OH$, 104-54-1; $H_2C{=}CHCH(Me)COC_4H_9$, 61122-64-3; $NaCo(CO)_4$, 14878-28-5; $Ni(CO)_4$, 13463-39-3; $PhCH_2MgCl$, 6921-34-2; (*E*)-$Ph\text{-}CH{=}CHCH_3$, 873-66-5; $PhCH{=}CHCH_2OAc$, 103-54-8; $PdCl_2(CH_3CN)_2$, 14592-56-4; $MeOCOCH_2CH{=}CHPh$, 24891-74-5; $[\pi\text{-}C_3H_5Co(CO)_2PPh_3]$, 12149-50-7.

Organometallic Compounds of the Lanthanides. 15.[1] Synthesis and X-ray Crystal Structure of Monomeric Alkyldicyclopentadienyllanthanide Compounds

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Dicyclopentadienyllutetium chloride reacts with organolithium compounds RLi [R = CH_3, C_2H_5, $i\text{-}C_3H_7$, C_4H_9, $t\text{-}C_4H_9$, $t\text{-}C_5H_{11}$, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, $C_6H_4\text{-}4\text{-}CH_3$, $C(C_6H_5)_3$], in tetrahydrofuran at −78 °C, to give monomeric alkyldicyclopentadienyllutetium derivatives, $Cp_2LuR{\cdot}THF$. Dicyclopentadienylsamarium *tert*-butoxide, prepared from $SmCl_3$, NaC_5H_5, and sodium *tert*-butoxide in THF, reacts with $LiCH_2Si(CH_3)_3$ with formation of dicyclopentadienyl(trimethylsilylmethyl)samarium. Analogous THF complexes, $Cp_2LnR{\cdot}THF$, have been prepared from $Cp_2LnCl{\cdot}THF$ and LiR, with Ln = Er and Yb and R = $t\text{-}C_4H_9$ and $CH_2Si(CH_3)_3$ and characterized by elemental analysis and IR spectra. From the reaction of $LuCl_3$, NaC_5H_5, and $NaBH_4$ in THF, dicyclopentadienyllutetium tetrahydroborate has been obtained. The new compounds have been characterized by elemental analyses and IR and NMR (^1H, ^{13}C) spectra. The structures of the complexes $(C_5H_5)_2LuCH_2Si(CH_3)_3{\cdot}THF$ and $(C_5H_5)_2LuC_6H_4\text{-}4\text{-}CH_3{\cdot}THF$ have been elucidated through complete X-ray analyses. The crystals of the first compound are orthorhombic with a = 1738.1 (8) pm, b = 1226.8 (3) pm, c = 917.0 (3) pm, space group $P2_12_12_1$, Z = 4, R = 0.058, and 2735 observed reflections. The crystals of the second compound are orthorhombic with a = 1581.4 (36) pm, b = 1251.1 (11) pm, c = 946.7 (19) pm, space group $Pnma$, Z = 4, R = 0.081, and 798 observed reflections.

Introduction

After the synthesis of the first organometallic compounds of the lanthanides, the tricyclopentadienyl complexes of Sc, Y, La, Ce, Pr, Nd, Sm, and Gd by Wilkinson and Birmingham in 1954,[2] interest in this part of the Periodic Table increased only slowly in the next 15 years but more and more rapidly in the last decade.[3] After the symmetrical tricyclopentadienyl compounds had been studied, attention turned to derivatives of the ionic π-bonded cyclopentadienyl complexes. Dicyclopentadienyllanthanide chlorides[4] and cyclopentadienyllanthanide dichlorides[5] have been used as starting materials for the synthesis of many such derivatives.

The first homoleptic organometallic compounds of the lanthanides with η Ln–C σ bonds were prepared by Hart and co-workers in 1970,[6] and further work on dicyclopentadienyllanthanide alkyls and aryls by Tsutsui and co-workers[7] initiated the extensive search for preparative routes to new organic derivatives of these metals and for an understanding of their structures and their chemistry.

Tsutsui[7] claimed a monomeric structure, $(C_5H_5)_2Ln\text{–}R$, for these alkyl and aryl derivatives, as well as for some other dicyclopentadienyllanthanide allyl[8] and alkynyl[9] compounds, but without experimental support for such formulations. In 1976, by an X-ray structural investigation of the ytterbium compound,[11] Lappert and co-workers[10] discovered that the methyl derivatives, $(C_5H_5)_2LnCH_3$, are dimeric, with an electron-deficient, three-center bonding involving two lanthanide metals and a methyl bridge. A similar methyl-bridged structure has been demonstrated in complexes of dicyclopentadienyllanthanide alkyls with trimethylaluminum, as shown by the same authors for $(C_5H_5)_2Yb(\mu\text{-}CH_3)_2Al(CH_3)_2$.[12] A monomeric alkyl or aryl derivative of a lanthanide metal of low coordination number and without bulky alkyl groups is known for scandium in the case of the complex $(C_5H_5)_2ScCH_3{\cdot}py$.[13]

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