Synthesis of Unsymmetrical Diallyl Ketones: The Palladium-Catalyzed Coupling of Allyl Halides with Allyltin Reagents in the Presence of Carbon Monoxide

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The palladium-catalyzed coupling of allyl halides with allyltin reagents under 3–6 atm of carbon monoxide at ambient temperatures gives the unsymmetrical diallyl ketones. Higher pressures of carbon monoxide give higher yields. The coupling reaction is mild enough that rearrangement of the β, γ-double bond into conjugation with the carbonyl does not take place readily. The catalyst that gives the highest yields of product is that which is introduced by the addition of dichlorobis(acetonitrile)palladium(II) and triphenylphosphine in a 2:1 ratio. Carbonylation of the allyl halide partner takes place at the least substituted allylic position in the π-allyl complex while coupling of the allyltin partner occurs without allylic rearrangement. A major side reaction is a homocoupling of the allyltin reagent to give a symmetrical diallyl ketone.

Although there are a number of stoichiometric reactions of transition-metal complexes that generate ketones[1] from carbon monoxide and organic reagents, the number of synthetically useful catalytic reactions of this type are few and only lately have such reactions appeared in greater number. Vinyl-[2] and arylmercury[3] reagents can be coupled in the presence of carbon monoxide by rhodium catalysts to yield the symmetrical divinyl or diaryl ketones. Also, the nickel-catalyzed reaction of phenylmagnesium bromide with bromobenzene under carbon monoxide yields benzophenone.[4]

The transition-metal-catalyzed coupling reactions of organic halides with organotin reagents in the presence of carbon monoxide have been developed more recently.[5] In most of these reactions hexamethylphosphoric triamide was the reaction solvent, and in most cases, relatively high reaction temperatures (~120 °C) and carbon monoxide pressures (20–30 atm) were utilized.[5a,b]
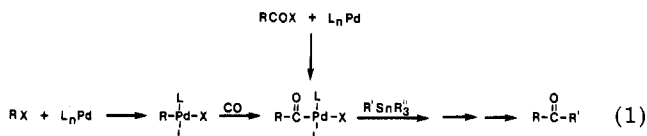
The direct coupling reactions of allyl halides with allyltin reagents catalyzed by palladium[6] or zinc chloride[7] have been shown to yield exclusively the cross-coupled products. In the palladium-catalyzed reaction, minimal allyl transposition takes place in the allyl halide partner, but predominant allylic rearrangement occurs in the tin reagent.[6] We have demonstrated that the palladium-catalyzed cross-coupling of allyl halides with aryl- and vinyltin reagents in the presence of carbon monoxide (1–3 atm) gives high yields of the unsymmetrical allyl vinyl or allyl aryl ketone.[8] The reaction conditions are mild, and the coupling tolerates a wide variety of functionality on either the allyl halide or the tin reagent. The success in this coupling reaction under mild conditions prompted us to

Table I. Diallyl Ketone Synthesis[a]

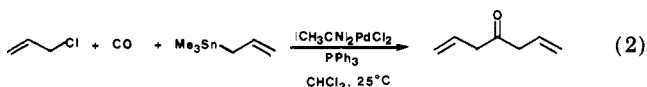| PPh$_3$:Pd	% conversion of allyltrimethyltin	% yield of diallyl ketone[b]
0:1	30	7
0.5:1	100	62
1:1		53
2:1	76	40

[a] PdCl$_2$(CH$_3$CN)$_2$, PPh$_3$, 3 atm of CO, CDCl$_3$, 22 °C, 48 h. [b] Determined by ^{1}H NMR using benzene as internal standard.

explore the carbonylative coupling reaction of allyl halides with allyltin reagents in an effort to develop a useful synthesis of unsymmetrical diallyl ketones. Such a coupling reaction for ketone synthesis holds the advantage over the palladium-catalyzed synthesis of ketones from acid chlorides and tin reagents[9] in that the acid chloride of one of the organic partners need not be prepared. Thus, other functionality in the coupling partners need not be protected. The overall catalytic strategy, therefore, relies on generation of the acylpalladium species in the cycle from an organic halide and carbon monoxide rather than from an acid chloride (eq 1).

$$RCOX + L_nPd$$
$$\downarrow$$
$$RX + L_nPd \longrightarrow R{-}\overset{L}{\underset{L}{Pd}}{-}X \xrightarrow{CO} R{-}\overset{O}{\overset{\|}{C}}{-}\overset{L}{\underset{L}{Pd}}{-}X \xrightarrow{R'SnR''_3} \longrightarrow \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}R' \quad (1)$$

Results and Discussion

The model reaction chosen for optimization in the synthesis of bisallylic ketones was the palladium-catalyzed carbonylation reaction between allyl chloride and allyl trimethyltin (eq 2). The conversion of the tin reagent and

$$\text{\Large /\!\!\!\!\diagdown\!\!\diagup Cl} + CO + Me_3Sn\diagdown\!\!\!\diagup\diagdown \xrightarrow[\text{PPh}_3]{\underset{\text{CHCl}_3,\,25°C}{|CH_3CN|_2PdCl_2}} \text{product} \quad (2)$$

the yield of 1,6-heptadiene-4-one was dependent on the

(1) See for example: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 482–491.

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(3) Bumagin, N. A.; Kalinovskii, I. O.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 221.

(4) Yamamoto, T.; Kohara, T.; Yamamoto, A. *Chem. Lett.* **1976**, 1217.

(5) (a) Tanaka, M. *Tetrahedron Lett.* **1979**, 2601; *Synthesis* **1981**, 47. (b) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1981**, *205*, C27. (c) Bumagin, N. A.; Bumagina, I. G.; Kashin, A. N.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1981**, *261*, 1141.

(6) Godschalx, J.; Stille, J. K. *Tetrahedron Lett.* **1980**, *21*, 2599.

(7) Godschalx, J. P.; Stille, J. K. *Tetrahedron Lett.* **1983**, *24*, 1905.

(8) Sheffy, F. K.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 7173. Sheffy, F. K.; Godschalx, J. P.; Stille, J. K., submitted for publication.

(9) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636; *J. Org. Chem.* **1979**, *44*, 1613. (b) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 669; **1983**, *105*, 6129. (c) Labadie, J. W.; Stille, J. K. *Tetrahedron Lett.* **1983**, *24*, 4283. (d) Labadie, J. W.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4634.

Table II. Carbonylative Coupling:
Allyl Chloride and Allyltrimethyltin[a]

solv	P, atm	additive	% yield[b]
CHCl$_3$	1		7
	3		62
	3	LiCl (2.0 equiv)	43
	6		75 (70)[c]
CH$_2$Cl$_2$	3		57
	3	LiCl (2.0 equiv)	58
	6		67
C$_6$H$_6$	6	LiCl (2.0 equiv)	66
			69
THF	6		18[d]
CHCl$_3$	6	ZnCl$_2$ (10 mol %)	0
		Li$_2$CO$_3$	72
		(structure)	0
		(structure)	50
		galvinoxyl (0.05 equiv)	64
		H$_2$O	47

[a] Reactions were carried out at 25 °C for 48 h with 1.5 mol % (CH$_3$CN)$_2$PdCl$_2$ and 0.75 mol % PPh$_3$. Increasing the amount of catalyst (3% and 7% Pd had no effect on the yield). [b] Yields were obtained from the ^{1}H NMR by integration against an internal standard, except where noted. [c] Isolated yield. [d] GC yield; benzene internal standard.

phosphine to palladium ratio, the optimum value being close to 0.5:1 (Ph$_3$P:Pd, Table I).

The use of THF in this reaction led to some double-bond isomerization into conjugation with the carbonyl group. Under these reaction conditions, no further addition of allyltin reagent to the ketone took place, an addition reaction known[10] to occur with certain allyltin reagents, usually at elevated temperatures or in the presence of Lewis acids. The addition of trimethyl- or tributylallyl tin reagents to α,β-unsaturated ketones takes place rapidly at low temperatures in the presence of Lewis acids.[11]

The coupling reaction (eq 2) also was carried out in several different solvents, at different carbon monoxide pressures, with excess tin reagent, and with a variety of additives (Table II). Higher carbon monoxide pressures improved the yield of ketone, but the reaction solvent or added lithium chloride had little effect. Protonic acids; for example, hydrogen chloride, which could be present in the reaction mixture, rapidly cleave allyltrimethyltin yielding trimethyltin chloride. A small excess of allyltrimethyltin reagent had no effect on the yield, while a larger excess decreased the yield of diallyl ketone. Passage of the chloroform solvent through basic alumina just prior to its use had no effect on the yield. The addition of lithium carbonate had little effect, while the addition of a hindered base, 2,6-di-*tert*-butylpyridine, shut down the

(10) (a) Daude, G.; Pereyre, M. *J. Organomet. Chem.* **1980**, *190*, 43. (b) Peruzzo, V.; Tagliavini, G. *Ibid.* **1978**, *162*, 37. (c) Peruzzo, V.; Tagliavini, G.; Gambaro, A. *Inorg. Chem. Acta* **1979**, *34*, L263. (d) Gambaro, A.; Peruzzo, V.; Plazzogna, G.; Tagliavini, G. *J. Organomet. Chem.* **1980**, *197*, 45. (e) Gambaro, A.; Marton, D.; Peruzzo, V.; Tagliavini, G. *Ibid.* **1981**, *204*, 191. (f) Mukaiyama, T.; Harada, T.; Shoda, S. *Chem. Lett.* **1980**, 1507. (g) Mukaiyama, T.; Harada, T. *Ibid.* **1981**, 1527. (h) Nokami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191.

(11) (a) Naruta, Y.; Maruyama, K. *Chem. Lett.* **1979**, 885. (b) Naruta, Y. *J. Am. Chem. Soc.* **1980**, *102*, 3774; *J. Org. Chem.* **1980**, *45*, 4097. (c) Maruyama, K.; Takuwa, A.; Naruta, Y.; Satao, K.; Soga, O. *Chem. Lett.* **1981**, 47. (d) Naruta, Y.; Uno, H.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1277.

reaction. A radical chain reaction apparently is involved neither in the coupling nor in possible adverse side reactions, since the addition of radical traps did not alter the yield appreciably.
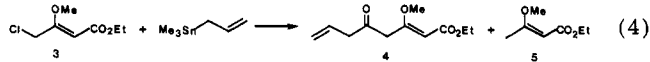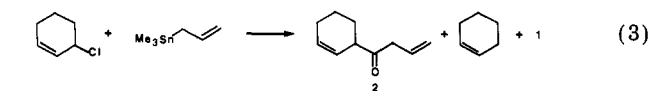
Several other experiments carried out, but not listed in Table II, should be mentioned. The reaction does not occur in the absence of a palladium catalyst. Other palladium catalysts were not as good; introduction of the catalyst as bis(dibenzylideneacetone)palladium(0), with triphenylphosphine (Pd:PPh$_3$ = 2:1, 6 atm of CO, CDCl$_3$) gave a 55% yield of product while use of diphos as a ligand nearly stopped the reactions (9%). The use of allyl mesylate instead of allyl chloride (THF or CHCl$_3$), even in the presence of molar equivalents of lithium chloride failed to give ketone. Allyl bromide did not give as high yields. Either allyltrimethyltin or allyltributyltin could be utilized equally well.

The generality of this reaction with other allyl chlorides and allyltin reagents was explored (Table III). The reaction is relatively slow; more than 24 h was needed for the reaction of prenyl chloride and allyltrimethyltin to go to completion. Yields obtained from the corresponding tributyltin reagent, although not shown in the table, were lower than those obtained from the trimethyltin reagent. The yields of ketone varied considerably depending on the allyl chloride and the allyltin reagent. Both crotyl chloride and 3-chloro-1-butene gave the same product (entries 4 and 5), demonstrating that the insertion of carbon monoxide in the allyl palladium complex is regioselective, taking place at the least hindered carbon. This is in contrast to the direct coupling reactions of allyl halides with allyltin reagents in which allylic rearrangement predominates in the allyltin partner[6] and is relatively insensitive to a steric effect.

In some reactions, particularly those with prenyl chloride (entry 3), double-bond migration into conjugation with the carbonyl group was observed and accounted for a significant percent of the product. The diallyl ketones could not be chromatographed on silica or even on neutral alumina without some double-bond migration taking place. In most cases, however, the products were stable under the reaction conditions.

A major side reaction was a carbonylative homocoupling reaction involving the allyltin reagent. In particular, in coupling reactions involving allyltrimethyltin, diallyl ketone was formed, the yields of this product approaching 30% in some cases. Thus, the consumption of as much as 60% of the tin reagent by this pathway in a number of reactions severely limited the yield of the desired product.
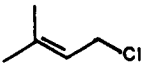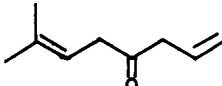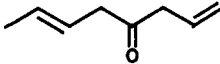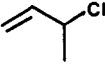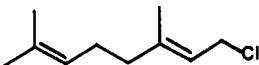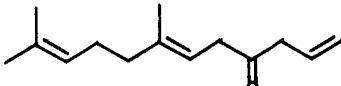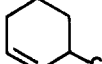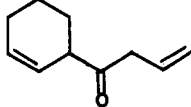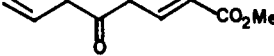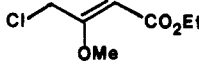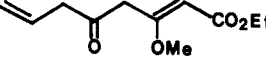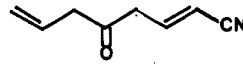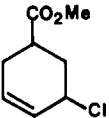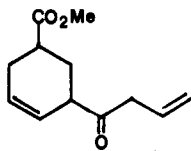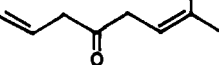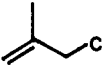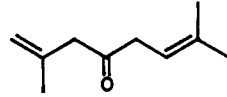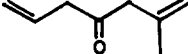
In certain coupling reactions, some of the byproducts of the reaction were identified. The coupling reaction of 3-chlorocyclohexene with allyltrimethyltin (entry 7) gave, in addition to a 27% yield of the desired ketone 2, a 13% yield of 1,6-heptadien-4-one (1) and cyclohexene (22%) (eq 3). The coupling of ethyl 4-chloro-3-methoxy-2-butenoate (3) produced 26% of 1,6-heptadien-4-one (1) and 29% of ethyl 3-methoxy-2-butenoate (5) in addition to the desired product 4 (eq 4). Other products obtained from these reactions were not identified.

$$\text{(eq 3)}$$

$$\text{(eq 4)}$$

Although both allylic chlorides and bromides would

Table III. Diallyl Ketone Synthesis[a]

entry	allyl chloride	allyltin	P, atm	product	% yield[b] product	1[d]
1	(prenyl chloride)	Me₃Sn—allyl	3	(product)	33	
2			6		47[c]	
3			6		54 (48)	33
4	(crotyl chloride)		6	(product)	35 (28)	
5	(α-methylallyl chloride)		3		20	
6	(geranyl chloride)		6	(product)	31 (22)	
7	(cyclohexenyl chloride)		6	(product)	21	13
8	Cl—CH=CH—CO₂Me		3	(product) CO₂Me	59	
9	Cl—C(OMe)=CH—CO₂Et		6	(product) CO₂Et, OMe	20	26
10	Br—CH=CH—CN		6	(product) CN	16	20
11	(cyclohexene, CO₂Me, Cl)		6	(product) CO₂Me	(23)	27
12	(allyl chloride)	Me₃Sn—prenyl	6	(product)	52 (47)	
13	(methallyl chloride)		3	(product)	27	
14	(allyl chloride)	n-Bu₃Sn—methallyl	6	(product)	32 (28)	

[a] Reactions were run in chloroform at 25 °C for 48 h with 1% $(CH_3CN)_2PdCl_2$ and PPh_3 $(Pd:PPh_3 = 2)$. [b] ¹H NMR yields (isolated yields). [c] The reaction was stopped after 24 h. [d] 1,6-Heptadien-4-one.

undergo the carbonylative coupling reaction, the bromides reacted much more slowly and gave lower yields. The reactions of chloro(η^3-prenyl)(triphenylphosphine)palladium (6a) and the bromo complex 6b with allyltrimethyltin under 3 atm of carbon monoxide showed a similar reactivity pattern, 6a reacting faster than 6b, both giving 7-methyl-1,6-octadien-4-one (eq 5). This difference in rates possibly reflects the rate of carbonylation of the palladium

complex, since the conversion of 6a to the corresponding ester in ethanol in the absence of allyltrimethyltin was faster than that for 6b.

$$\text{(prenyl)Pd}\underset{X}{\overset{PPh_3}{\diagdown}} + Me_3Sn\text{—allyl} \longrightarrow \text{(product)} \qquad (5)$$

6a X = Cl
b X = Br
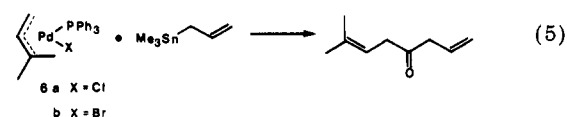
Experimental Section

Tetrahydrofuran and benzene were freshly distilled under nitrogen from sodium benzophenone prior to use. Chloroform and methylene chloride were passed through a short, basic alumina column just prior to use in the coupling reactions. Gas chromatographic analyses were carried out on Varian Models 3700 and 1520. Preparative gas chromatography was carried out on a Varian Model 1520. Radial chromatography was carried out with a Chromatotron (Harrison Research Co.). The ^{1}H NMR spectra were obtained on a Varian EM-360, JEOL FX-100, or IBM WP-270 spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX-100 or IBM WP-270 instrument.

Tin Reagents. The following tin reagents were prepared according to the literature procedure: allyltrimethyltin,[12] allyltributyltin,[13] prenyltrimethyltin,[14] prenyltributyltin,[15] and methallyltributyltin.[16]

Allyl Halides. Allyl halides either were obtained commercially or were prepared according to the literature procedure: crotyl chloride,[17] geranyl chloride,[18] 3-chlorocyclohexene,[19] methyl-4-chloro-2-butenoate,[20] ethyl 4-chloro-3-methoxy-2-butenoate (3),[21] 4-bromo-2-butenonitrile,[22] and 3-chloro-5-carbomethoxycyclohexene.[23]

General Procedure for Palladium-Catalyzed Allyl–Allyl Carbonylation Reactions. To a Fischer-Porter tube under argon were added 26 mg (0.10 mmol) of dichlorobis(acetonitrile)palladium(II),[24] 12 mg (0.05 mmol) of triphenylphosphine, and 2.5 mL of CHCl$_3$ or CDCl$_3$ (when the yields were to be determined directly by ^{1}H NMR) that has been freshly filtered through basic alumina. The mixture was stirred until it became homogeneous and was red-orange (~10 min). To this solution was added 5 or 10 mmol of an allyl halide followed by 5 or 10 mmol of an allyltin reagent and 2.5 mL additional CDCl$_3$ or CHCl$_3$ when 10 mmol of the reagents were used. The tube was then connected to a Fischer-Porter pressure head (fitted with a pressure release valve adjusted to 125 psig). The tube was pressurized to 3 atm, and then the pressure was released. The tube was flushed in this manner two more times and then repressured to 3 or 6 atm with carbon monoxide. The reaction mixture was stirred at ambient temperature for 24 or 48 h after which time, palladium black often had formed. The pressure was slowly released, 100 mg of benzene was added as an internal standard, and the sample was analyzed by ^{1}H NMR and GC (capillary column).

When the tin reagent was a trimethyltin compound, isolation of the product was accomplished as follows. The reaction mixture was diluted with diethyl ether and washed with three 15-mL portions of water and then with brine. The ether layer was dried over sodium sulfate, and the filtrate was concentrated by distillation of the ether. The products were isolated by column chromatography, radial chromatography or preparative GC. When the tin reagent was a tributyltin compound, the crude reaction mixture was chromatographed on a column or subjected to preparative GC.

1,6-Heptadien-4-one. This compound was isolated from the reaction mixture by column chromatography on silica gel: ^{1}H NMR (CDCl$_3$) δ 3.08 (d of m, 4 H, J = 7 Hz), 5.00 (m, 4 H), 5.75 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 46.17, 117.52, 129.84, 204.28; MS m/e 110.0694; calcd for C$_7$H$_{10}$O 110.0731.

7-Methyl-1,6-octadien-4-one. This compound was isolated from the reaction mixture by preparative GC: ^{1}H NMR (CDCl$_3$) δ 1.49 (s, 3 H), 1.60 (d, 3 H, J = 1 Hz), 3.03 (m, 4 H), 5.0 (m, 3 H), 5.8 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 17.5, 25.2, 41.5, 46.5, 115.2, 117.8, 130.2, 135.0, 205.9. Anal. Calcd for C$_9$H$_{14}$O: C, 78.21; H, 10.21. Found: C, 77.42; H, 10.42.

1,6-Octadien-4-one. This compound was isolated from the reaction mixture by column chromatography on silica gel: ^{1}H NMR (CDCl$_3$) δ 1.57 (m, 3 H), 3.09 (d of m, 4 H, J = 7 Hz), 4.95 (m, 2 H), 5.7 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 17.4, 45.5, 46.4, 117.9, 122.4, 128.7, 129.9, 205.4; MS, m/e 124.0867, calcd for C$_8$H$_{12}$O 124.0888.

7,11-Dimethyl-1,6,10-dodecatrien-5-one. This compound was isolated from the reaction mixture by preparative GC: ^{1}H NMR (CDCl$_3$) δ 1.52–1.59 (2s, 9 H), 1.98 (m, 4 H), 3.08 (m, 4 H), 5.10 (m, 4 H), 5.8 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 16.0, 17.3, 25.3, 26.1, 39.3, 41.7, 46.6, 115.3, 117.9, 123.3, 123.5, 130.3, 138.7, 205.7; MS, m/e 206.1659; calcd for C$_{14}$H$_{22}$O 206.1670.

2-Cyclohexenyl Allyl Ketone. This compound was isolated by flash chromatography on silica gel: ^{1}H NMR (CDCl$_3$) δ 2.05 (m, 6 H), 3.20 (m, 3 H), 5.15 (m, 2 H), 5.76 (m, 1 H), 5.88 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 20.5, 24.5, 45.1, 48.4, 49.4, 118.1, 123.7, 129.6, 130.7, 208.9. Anal. Calcd for C$_{10}$H$_{14}$O: C, 79.96; H, 9.39. Found: C, 79.90; H, 9.41.

Methyl 5-Oxo-2,7-octadienoate. The ^{1}H NMR spectrum of the crude product was consistent with the allyl ketone structure. The compound could not be obtained pure enough to obtain a clean ^{1}H spectrum: ^{1}H NMR (CDCl$_3$) δ 2.96 (d, 2 H), 3.05 (d, 2 H), 3.55 (s, 3 H), 5.08 (m, 2 H), 5.45–5.85 (m, unresolved, 3 H).

Ethyl 3-Methoxy-5-oxo-2,7-octadienoate (4). This compound was isolated by preparative GC: ^{1}H NMR (CDCl$_3$) δ 1.35 (t, 3 H, J = 7 Hz), 3.06 (m, 2 H), 3.66 (s, 2 H), 3.79 (s, 3 H), 4.24 (q, 2 H, J = 7 Hz), 5.08 (m, 2 H), 5.18 (s, 1 H), 5.70 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 13.9, 45.7, 53.2, 55.6, 59.5, 95.2, 116.1, 128.9, 165.9, 168.5, 204.7. Anal. Calcd for C$_{11}$H$_{16}$O: C, 62.25; H, 7.60. Found: C, 62.07; H, 7.64. Ethyl 3-methoxy-2-butenoate (5) also was isolated by GC and was identical with an authentic sample.[21]

5-Oxo-2,7-octadienonitrile. This compound was isolated by preparative GC: ^{1}H NMR (CDCl$_3$) δ 3.05 (m, 4 H), 5.03 (m, 2 H), 5.36 (m, 1 H), 5.73 (m, 1 H), 6.53 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 46.6, 51.8, 113.7, 116.2, 129.3, 131.5, 145.3, 205.9. Anal. Calcd for C$_8$H$_9$NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.08; H, 6.75; N, 10.36.

Methyl 3-(But-3-enoyl)-1-cyclohex-4-enecarboxylate (2). This compound was isolated by preparative GC: ^{1}H NMR (CDCl$_3$) δ 1.90–2.35 (m, 5 H), 3.17, (m, 3 H), 3.65 (s, 3 H), 5.15 (m, 2 H), 5.52 (m, 2 H), 5.75 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 27.2, 33.9, 34.3, 47.8, 53.5, 54.0, 118.1, 127.1, 128.9, 129.0, 174.7, 209.2. Anal. Calcd for C$_{12}$H$_{16}$O$_3$: C, 69.21; H, 7.74. Found: C, 69.09; H, 7.84.

2,7-Dimethyl-1,6-octadien-4-one. This compound was isolated from the reaction mixture by column chromatography on silica gel: ^{1}H NMR (CDCl$_3$) δ 1.55 (s, 3 H), 1.68 (s, 6 H), 2.94 (m, 4 H), 4.58 (m, 2 H), 4.90 (t, 1 H); ^{13}C NMR (CDCl$_3$) δ 17.7, 22.3, 25.4, 41.5, 51.2, 114.3, 115.6, 135.0, 138.8, 206.1; MS, m/e 152.1203, calcd for C$_{10}$H$_{16}$O 152.1201.

2-Methyl-1,6-heptadien-4-one. This compound was isolated by radial chromatography: ^{1}H NMR (CDCl$_3$) δ 1.53 (s, 3 H), 2.99 (m, 4 H), 4.57 (m, 2 H), 5.02 (m, 2 H), 5.69 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 22.1, 46.8, 50.8, 114.6, 118.3, 130.2, 138.8, 205.4. Anal. Calcd for C$_8$H$_{12}$O: C, 77.31; H, 9.74. Found: C, 77.36; H, 9.72.

Bromo- (6b) and Chloroprenyl(triphenylphosphine)palladium(II) (6a). These compounds were prepared by the addition of triphenylphosphine to the prenylpalladium bromide or chloride dimer.[25] Carbonylative coupling reactions with allyltrimethyltin were carried out in chloroform under 6 atm carbon monoxide according to the general procedure.

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Correlations of Acetylenic and Carbonyl Stretching Frequencies in the (μ-Alkyne)hexacarbonyldicobalt Complexes. Evaluation of σ- and π-Bonding between Alkyne and Metal

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The ν(C≡C) stretching frequencies of a great variety of (μ-alkyne)hexacarbonyldicobalt complexes, (μ-RC≡CR')Co$_2$(CO)$_6$, have been determined unambiguously and their variations on coordination related to the electronic nature of the substituents R and R'. Three linear relationships have been observed depending on the number of acceptor groups. Examination of the average carbonyl value of ν(C≡O) in these complexes also indicates the existence of the same classes, and, thus, these correlations combined with a stabilization on complexation are very useful to predict unknown frequencies. A combination of the changes $\Delta\nu$(C≡C), which measure $\sigma + \pi$ transfers, and the changes $\Delta\nu$(C≡O), which measure $\sigma - \pi$ transfers, allows separation of the σ- and π-components of the interaction between alkyne and metal.

Introduction

The molecular structures of numerous olefin and acetylene complexes have been investigated by X-ray techniques, however, a limited number of structural studies of (μ-acetylene)hexacarbonyldicobalt complexes are available.[1] The striking features to notice in these last examples are a cis bending of the alkyne substituents toward the configuration of the first excited state (with the Co—Co and C≡C bonds perpendicular to each other but not in the same plane) and a lengthening of the acetylenic triple bond with a concomitant drop in bond order. This lengthening is a direct consequence of synergic σ–π interactions and electron transfer.[2] More information on this point can be obtained by examining the frequencies and intensities of ν(C≡C) vibrations. Thus, an analysis of vibrational frequencies in the series of complexes (RC≡CR')Co$_2$(CO)$_6$ should provide considerable insight into the molecular structures and metal–ligand bonding.

Infrared spectroscopic studies of acetylene derivatives (RC≡CR)Co$_2$(CO)$_6$ have, to date, been limited largely to the ν(C≡O) region.[3–12] Only Dickson[13–17] and Iwashita[18–20]

have examined ν(C≡C) vibrations in this type of complex. In particular, Iwashita has precisely determined the vibrational frequencies ν(C≡C) for the complexes (RC≡CR)Co$_2$(CO)$_6$ (R = R' = H; R = H, R' = D; R = R' = D; R = H, R' = CH$_3$; R = D, R' = CH$_3$; R = R' = CH$_3$).

In the present study a wide range of derivatives having substituents with electron-donating or-accepting properties have been analyzed in detail with the goal of correlating for the first time changes in ν(C≡C) and ν(C≡O) and using these changes as a probe of electronic structure. Thus, an evaluation of the effects of σ- and π-transfer between the alkyne and the cobalt atom has been carried out. Furthermore, correlations of the type described here have allowed an assignment of ν(C≡C) frequencies for

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