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Carbonylation of the A-Frame Complex $Rh_2(\mu\text{-}CO)(CH_2C_6H_5)_2(dppm)_2$. Formation of the Dicarbonylated Product via a Radical Pathway

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Summary: The dibenzyl A-frame compound $Rh_2(\mu\text{-}CO)(CH_2C_6H_5)_2(dppm)_2$ is prepared by the reaction of benzylmagnesium chloride with $Rh_2Cl_2(CO)_2(dppm)_2$. The compound undergoes carbonylation leading to mono- and dicarbonylated products depending on CO pressure. At 300 Torr (0.4 atm) of CO, the major product is the monoketone 1,3-diphenylacetone, while, at 2.5 atm of CO, clean conversion to dicarbonylated product is observed. An intermolecular mechanism for dicarbonylation is shown by a crossover experiment, and radical involvement is demonstrated through the use of an H-atom donor during carbonylation, yielding phenylacetaldehyde as the major organic product.

Carbonylation is one of the most important and extensively studied reactions of metal–carbon bonds. While numerous reports of single carbonylation exist,[1] examples of double carbonylation remain relatively rare and have been observed mainly through the use of Pd complexes, leading to the formation of α-keto esters and amides.[2] There have also been a few reports describing α-dione formation.[3] Recently, we reported the carbonylation of the methyl A-frame complex $Rh_2(\mu\text{-}CO)(CH_3)_2(dppm)_2$ (**1**; dppm = bis(diphenylphosphino)methane), which at ambient temperature and low CO pressure results in the formation of acetone, butanedione, and the tricarbonyl complex $Rh_2(CO)_3(dppm)_2$ (**2**).[4] The relative amounts of the organic products were observed to be extremely sensitive to CO pressure, with acetone being predominant at 50 Torr and butanedione being the major product (<90%) at ca. 760 Torr. Mechanistic studies revealed that the two organic products were formed via completely separate pathways, with the dione arising by acetyl radical coupling.[4] In this report we describe another example of double carbonylation using the related benzyl A-frame complex $Rh_2(\mu\text{-}CO)(CH_2C_6H_5)_2(dppm)_2$ (**3**), which also proceeds by an intermolecular radical pathway. This result of acyl coupling is extraordinary under the low CO pressures employed because the phenylacetyl radical, $PhCH_2(O)C^{\bullet}$, is known to decarbonylate very rapidly.[5]

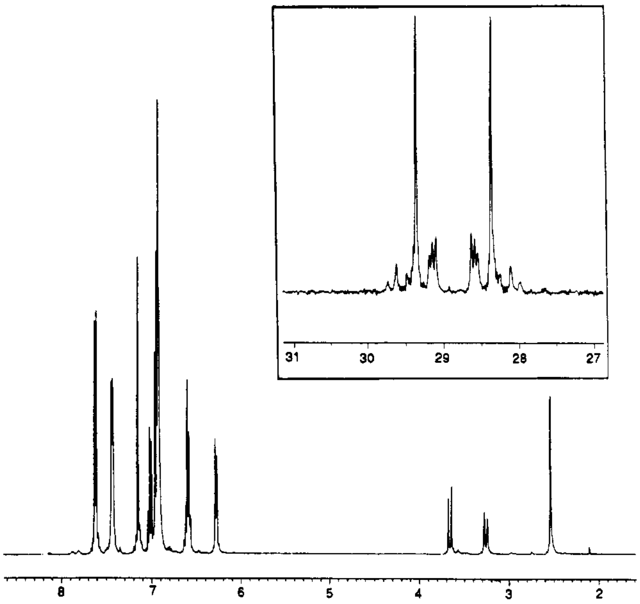

Figure 1. $^1H\{^{31}P\}$ NMR spectrum in C_6D_6 of $Rh_2(\mu\text{-}CO)(CH_2C_6H_5)_2(dppm)_2$ (**3**). The inset shows the $^{31}P\{^1H\}$ spectrum.

Complex **3** was synthesized by the reaction of excess benzylmagnesium chloride with $Rh_2Cl_2(CO)_2(dppm)_2$ (**4**)[6] in THF at −75 °C under N_2 and recrystallized from benzene or toluene. The resultant product is orange, air-sensitive, and soluble in THF, benzene, methylene chloride, and toluene. Characterization of **3** was performed by ^1H and ^{31}P NMR and infrared spectroscopy. The ^1H NMR spectrum of **3** reveals the benzylic protons as a broad single at δ 2.5 ppm (4 H) with unresolvable J_{HP} couplings and the dppm $-CH_2-$ protons as two inequivalent doublets of multiplets at δ 3.25 (2 H) and 3.65 ppm (2 H). Upon ^{31}P decoupling, the benzylic proton resonance changes to a sharp singlet while the dppm $-CH_2-$ resonances become simple doublets (J_{HH} = 14 Hz), as shown in Figure 1. The

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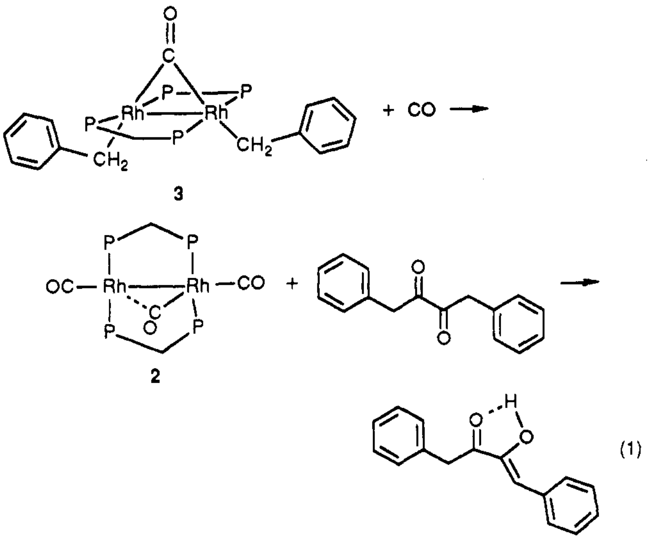
phenyl region of the spectrum contains resonances at δ 7.4 (8 H) and 7.6 ppm (8 H) for the dppm ortho protons, at δ 6.8–7.0 ppm (24 H) for the dppm meta + para protons, and at δ 6.2 (4 H) and 6.6 (6 H) ppm for the benzyl ortho and meta + para protons, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **3**, shown as the inset in Figure 1, exhibits a symmetric second-order pattern (AA′XX′X″X‴) nearly identical with that of methyl analog **1**, consistent with a large $^2J_{P-P}$ coupling and a trans disposition of phosphine donors.[4] The infrared spectrum exhibits a bridging ν(CO) band at 1746 cm^{-1} and no terminal CO stretches. All of these results indicate that **3** has an A-frame structure similar to that of **1**.

Compound **3** reacts with CO at low pressure and ambient temperature to give organic carbonyl compounds and $Rh_2(CO)_3(dppm)_2$ (**2**) as the sole metal-containing product. At 300 Torr (0.4 atm) of CO, the organic carbonylation product is primarily dibenzyl ketone, while at 2.5 atm of CO, dicarbonylation is the principal reaction pathway, leading to the initial formation of 1,4-diphenyl-2,3-butanedione as in eq 1. This dione rapidly tautomerizes to the more stable enol form 1,4-diphenyl-3-hydroxy-3-butene-2-one,[7] as evidenced by singlet resonances which grow in at δ 3.45, 3.70, and 6.20 ppm in C_6D_6. These resonances are integrated as 2:1:1 and are assigned to the benzyl methylene protons, the hydroxyl proton, and the enolic vinyl proton, respectively. When D_2O is added to the sample, the resonance at δ 3.70 ppm disappears within minutes, while the methylene and vinyl proton resonances become greatly diminished after 24 h. This facile H/D exchange upon addition of D_2O is readily explained by the tautomeric equilibrium between the dione and its corresponding enol. Further support for the identification of the enol product is obtained when the carbonylation is performed using ^{13}CO. Through $^{13}C\{^1H\}$ NMR spectroscopy, resonances at δ 195 and 147 ppm are observed for the carbonyl and enolic carbons, respectively, with $^1J_{C-C}$ = 55 Hz.



The reaction solution under 2.5 atm of CO shows that **3** converts initially to a single species. This intermediate exhibits a simple triplet for the methylene protons of the dppm ligand at δ 3.65 ppm (t, J_{P-H} = 18 Hz, 4 H) and a resonance at 4.35 ppm (s, 4 H) attributable to the benzyl protons of a phenylacetyl ligand. Employment of ^{13}CO in the reaction leads to the latter resonance being split by 4.0 Hz, corresponding to $^2J_{C-H}$. This intermediate is thus assigned as a symmetrical bis(phenylacetyl) species having the formula $Rh_2(C(O)CH_2C_6H_5)_2(CO)_x(dppm)_2$, and it disappears as the tricarbonyl complex $Rh_2(CO)_3(dppm)_2$ (**2**) and the initially produced dione are observed to form.

Despite the presence of a bis(acyl) intermediate, the reaction pathway leading to dicarbonylated products involves an intermolecular mechanism. When $Rh_2(\mu\text{-}CO)(CH_2Ph)_2(dppm)_2$ (**3**) is carbonylated under 1.5 atm of CO in the presence of excess $Rh_2(\mu\text{-}CO)(CH_3)_2(dppm)_2$ (**1**), the major reaction product is 3-hydroxy-4-phenyl-3-buten-2-one,[7,8] formed by the coupling of $PhCH_2CO^{\bullet}$ and $CH_3CO^{\bullet}$ radicals followed by tautomerism.[9] The only other organic product is 2,3-butanedione, and the sole metal-containing complex is $Rh_2(CO)_3(dppm)_2$ (**2**). There is no 3-hydroxy-1,4-diphenyl-3-buten-2-one or 1,3-diphenylacetone formed.

To provide confirmation of a radical pathway during carbonylation of **3**, the reaction was performed in the presence of a larger excess of either tris(trimethylsilyl)silane or triethylsilane as an H atom source. The use of a tris(alkyl)silane in this capacity appears valid, since any reaction of **3** directly with the silane is very slow (>24 h) compared to the carbonylation chemistry under study (<1 h). Under this set of conditions, the only organic product observed by ^1H NMR spectroscopy was phenylacetaldehyde. No other organic carbonylation products were seen.

The intermediacy of the phenylacetyl radical in the chemistry leading to dicarbonylation is interesting, because the phenylacetyl radical has been reported by Ingold to decarbonylate with a rate constant of 10^7 s^{-1}.[5] Under the conditions of the present study—i.e., 2.5 atm of CO pressure—it would be expected that significant decarbonylation would occur during the course of the reaction. While this is not observed at ambient room temperature, evidence for $PhCH_2CO^{\bullet}$ decarbonylation is obtained when the reaction is carried out at 92 °C, leading to dibenzyl ketone and bibenzyl as the major organic products. However, some dicarbonylation product is still seen to form. In a control experiment, it was shown that production of dibenzyl ketone and bibenzyl did not occur from the dicarbonylated product when a sample of **3**, previously reacted with CO at ambient temperature according to eq 1, was heated to 92 °C.

While the evidence for radical involvement in the dicarbonylation chemistry of $Rh_2(\mu\text{-}CO)(CH_2C_6H_5)_2(dppm)_2$ (**3**) is compelling, especially in light of the previous and totally consistent results of the methyl analog **1**, the actual mechanism of dione formation remains to be established. The reported rate of $PhCH_2CO^{\bullet}$ decarbonylation mitigates against a simple radical–radical coupling reaction for dione formation since the radical concentration is exceedingly small during carbonylation and yet the room-temperature reaction proceeds cleanly to the dione product. The results to date appear more consistent with a radical chain mechanism in which an acyl radical reacts with the intermediate bis(acyl) complex to generate dione and a binuclear acyl odd-electron species which can continue the chain through Rh–acyl bond homolysis. The resultant $Rh_2(CO)_x(dppm)_2$ species then adds CO to generate the only metal-containing product in the reaction, **2**. Studies to prove this proposal, which suggests a special role for bi-

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and polynuclear complexes in radical-driven carbonylation reactions, are in progress.

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New Palladium Complexes of Cis-Fixed Bidentate Nitrogen Ligands as Catalysts for Carbon–Carbon Bond Formation

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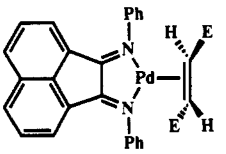
Summary: **New palladium complexes of the cis-fixed bidentate nitrogen ligand bis(phenylimino)acenaphthene (Ph-BIAN) are excellent catalysts for the carbon–carbon coupling reactions between various organic halides and organomagnesium, -zinc, and -tin reagents.**

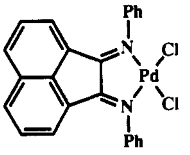
The palladium-catalyzed cross-coupling reaction has become a versatile tool in organic synthesis, and a wide variety of organic electrophiles and transmetalating reagents can be used.[1] The nature of the ligands coordinated to the palladium center is expected to have a pronounced influence on the carbon–carbon cross-coupling reaction, because it has been shown that oxidative addition[2] and reductive elimination[3] (and probably also transmetalation) are strongly dependent on the type of ligands coordinated to the metal center. So far, in such catalytic reactions, mainly monodentate phosphine complexes of palladium have been employed. Bidentate chelating phosphine ligands have been used in Grignard cross-coupling reactions,[1a] but in tin cross coupling they usually slow down the reaction rate,[4] although improved rates have also been reported.[5]

The few reports dealing with carbon–carbon bond formation catalyzed by palladium complexes of bidentate nitrogen ligands include nucleophilic allylic substitution[6] and coupling reactions of organic halides with organotin reagents catalyzed by Pd(2,2′-bipyridine)[7] or Pd(bis(2-pyridyl)silane).[8] Stoichiometric formation of a carbon–carbon-coupled product from various Pd(α-diimine)(η^3-allyl) complexes[9] and (isolated) Pd(IV) complexes[10] has also been reported.

We recently started investigations concerning the reactivity and catalytic activity of zerovalent (1) and divalent (2) palladium complexes containing the cis-fixed bidentate nitrogen ligands bis(arylimino)acenaphthene (e.g. Ph-BIAN).[11] Because of their good σ-donor and π-acceptor capacities and their rigidity, imposing a fixed cis orientation of both nitrogen atoms, we expected these ligands to endow properties upon the palladium center which might be favorable in carbon–carbon cross-coupling reactions. Both higher and lower oxidation states, necessary in an alternating sequence of oxidative addition and reductive elimination, can be stabilized. Furthermore, the diorganopalladium(II) complex formed after transmetalation has both organic groups in a fixed cis orientation, facilitating reductive elimination from this type of complex. Apart from the anticipated behavior it appears, to our surprise, that zerovalent [Pd(Ar-BIAN)(alkene)] complexes are also active as catalysts in the homogeneous hydrogenation of electron-poor alkenes.[12]



1 (E = CO_2CH_3)



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We wish to report that palladium complexes of the types 1 and 2 are indeed active in a variety of carbon–carbon bond-forming reactions under mild conditions using several organic electrophiles (including acyl, aryl, benzyl, vinyl, and 1,2-dienyl halides) with organomagnesium, -zinc, and -tin reagents.[13,14]

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