

with carbon monoxide. Gas was slowly absorbed. After reacting overnight, about 42 ml was taken up. The solvent was removed under reduced pressure and the crude product recrystallized twice from aqueous ethanol. There was obtained 0.12 g (12%) of off-white crystals, mp 136.0–136.5°, of 2-carbomethoxyhydrazobenzene. The compound had a carbonyl absorption band at 1690 cm^{-1} in chloroform solution.

Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$: C, 69.40; H, 5.82; N, 11.57. Found: C, 69.00; H, 6.14; N, 11.56.

A similar reaction of 0.64 g (1 mmole) of chloro-2-(phenylazo)-phenylpalladium in 20 ml of methanol under 40 psi of carbon monoxide at room temperature gave, after evaporation of the solvent

and recrystallization from aqueous ethanol, 0.07 g (17%) of 2-phenyl-1H-indazolone, mp 203–204° (lit.² 204°). The compound in chloroform solution had a carbonyl absorption band at 1680 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.65; H, 5.23; N, 12.61.

A similar reaction with chloro-2-(3-methylphenylazo)-4-methylphenylpalladium gave 0.12 g (25%) of 2-(3-methylphenyl)-6-methyl-1H-indazolone, mp 222–223°. The compound had a carbonyl absorption band at 1670 cm^{-1} in chloroform.

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{ON}_2$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.42; H, 5.92; N, 11.62.

π -Allylic Ligand Transfer Reactions between Cobalt and Palladium Complexes

Richard F. Heck

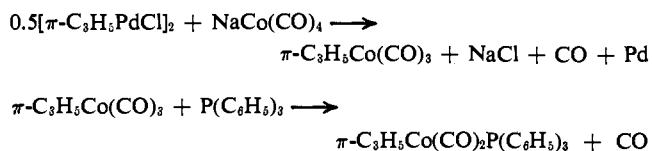
Contribution from the Research Center, Hercules Incorporated, Wilmington, Delaware 19899. Received July 13, 1967

Abstract: Sodium tetracarbonylcobaltate reacts with chloro- π -allylpalladium dimers to form tricarbonyl- π -allylcobalt derivatives. Lithium chloropalladate reacts with tricarbonyl- π -allylcobalt derivatives to form chloro- π -allylpalladium dimers.

The previous discovery that 2-(phenylazo)phenyl groups could be transferred from palladium to several different transition metal carbonyl anions¹ suggested that π -allylic groups might be transferred from palladium to other metal carbonyl anions in the same manner. Such a reaction would be useful for the preparation of new π -allylic complexes because several of the known methods for preparing these complexes are specific for a single metal. This paper reports an investigation of this reaction and π -allylic transfer reactions between cobalt and palladium complexes.

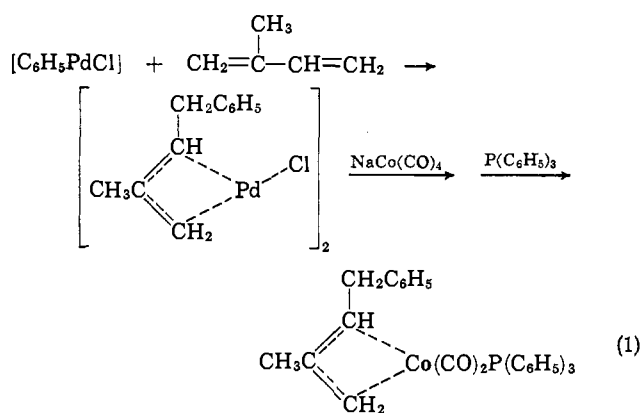
Results and Discussion

π -Allylic ligands are readily transferred from π -allylic palladium halides to tetracarbonylcobalt anion. Thus, chloro- π -allylpalladium dimer and sodium tetracarbonylcobaltate react in ether solution at room temperature to form tricarbonyl- π -allylcobalt, isolated as its monotriphenylphosphine derivative in 50% yield.



Of more interest are examples of the above reaction in which the π -allylic cobalt derivative cannot be conveniently prepared directly. For example, "phenylpalladium chloride" prepared by the exchange reaction from phenylmercuric chloride and lithium tetrachloropalladate, in the presence of isoprene, forms chloro-1-

benzyl-2-methyl- π -allylpalladium dimer.² The last compound undergoes the exchange reaction with $\text{NaCo}(\text{CO})_4$ producing tricarbonyl-1-benzyl-2-methyl- π -allylcobalt, isolated as the monotriphenylphosphine derivative, in 41% yield (eq 1). The π -allylic cobalt



compound formed cannot be obtained directly by reactions analogous to those used for preparing the π -allylic palladium compound.

Palladium chloride reacts directly with olefins under some conditions to produce π -allylic complexes.³ Cobalt derivatives do not react this way. Thus, numerous new π -allylic cobalt derivatives can be obtained indirectly by the ligand-exchange reaction. Mesityl oxide, for example, reacts with palladium chloride to form chloro-1-acetyl-2-methyl- π -allylpalladium,⁴ and

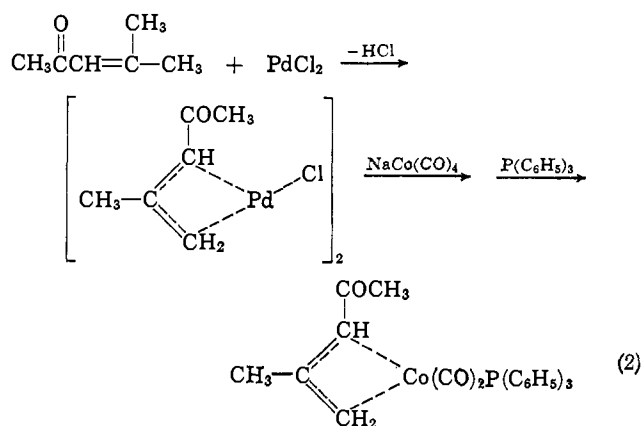
(2) R. F. Heck, unpublished work.

(3) R. Hüttel and H. Christ, *Chem. Ber.*, **96**, 3101 (1963).

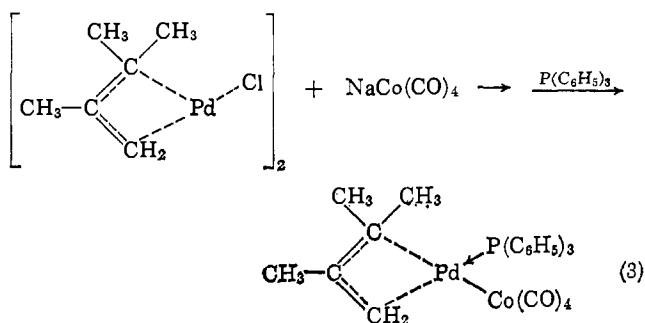
(4) G. W. Parshall and G. Wilkinson, *Chem. Ind. (London)*, 261 (1962).

(1) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 313 (1968).

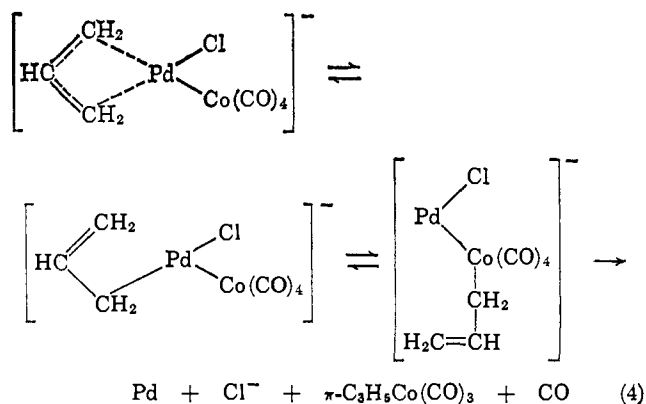
this complex reacts with $\text{NaCo}(\text{CO})_4$ to form the π -allylic cobalt derivative. This product was isolated as the monotriphenylphosphine derivative in 35% yield (eq 2).



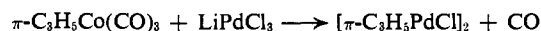
Another example of this reaction was investigated employing chloro-1,1,2-trimethyl- π -allylpalladium dimer, obtained from 2,3-dimethyl-2-butene and palladium chloride,⁸ and $\text{NaCo}(\text{CO})_4$. Under the same conditions as were used in the previous example, a palladium- and cobalt-containing compound was isolated. The brown crystalline product, isolated as a triphenylphosphine derivative in 6.5% yield, was rather unstable and insoluble so that a meaningful nmr spectrum could not be obtained. Probably, judging from the elemental analysis, the product is a simple substitution product where $\text{Co}(\text{CO})_4$ has replaced one chloro group, and a triphenylphosphine has replaced the bridging chloro group (eq 3). One could easily



imagine a mechanism for the π -allylic exchange reaction involving the formation of a palladium-metal-bonded intermediate which then undergoes a 1,2 shift of the allyl group probably *via* σ -carbon-bonded intermediates (eq 4).



Certain π -allylic cobalt derivatives can be readily obtained by reactions that are not applicable to palladium compounds. A π -allylic ligand transfer from cobalt to palladium, therefore, could be of use in preparing some π -allylpalladium derivatives. It was found that tricarbonyl- π -allylcobalt reacts with lithium trichloropalladate in acetonitrile solution with CO evolution to form chloro- π -allylpalladium dimer in 22% yield.



Similarly, chloro-1,3-dimethyl- π -allylpalladium dimer was prepared from tricarbonyl-1,3-dimethyl- π -allylcobalt in 16% yield. Unfortunately, three types of ligands which can easily be obtained in cobalt complexes and not in palladium complexes did not produce stable π -allylic palladium derivatives. Tricarbonyl-1-acetylmethyl- π -allylcobalt, prepared from tetracarbonylmethylcobalt and butadiene,⁵ reacted readily with LiPdCl_3 , but no stable π -allylic palladium compound could be isolated from the reaction mixture. Similarly, tricarbonyl-2,3-diethyl- π -(2,4)-(penteno-4-lactonyl)cobalt, obtained by the reaction of 3-hexyne with tetracarbonylmethylcobalt,⁶ reacted with lithium trichloropalladate, but the product could not be isolated. Finally, tricarbonyl-1-acetoxy- π -allylcobalt, from acrolein and tetracarbonylmethylcobalt,⁷ was allowed to react with lithium trichloropalladate, but, again, the product was too unstable to be isolated.

Experimental Section

Dicarbonyltriphenylphosphine- π -allylcobalt from Chloro- π -allylpalladium Dimer. A mixture of 0.182 g (0.5 mmole) of $[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2$ ⁹ and 15 ml of 0.07 M $\text{NaCo}(\text{CO})_4$ in ether⁹ was stirred at room temperature under nitrogen for 1 hr. Gas evolved and a black precipitate appeared during the reaction. An infrared spectrum of the solution showed absorptions at 2000 and 2070 cm^{-1} . The latter bands are characteristic of tricarbonyl- π -allylcobalt.¹⁰ Then 1.5 ml of 1.0 M triphenylphosphine in ether was added. After stirring at room temperature for about 1 hr, the mixture was centrifuged and the clear yellow solution obtained was concentrated under reduced pressure to about 5 ml. On cooling in Dry Ice, yellow crystals of dicarbonyltriphenylphosphine- π -allylcobalt were obtained. The crystals were separated by centrifuging and dried under reduced pressure. There was obtained 0.21 g (50%) of yellow-orange prisms of the product, mp 119° dec, whose infrared spectrum was identical with that of the authentic material.¹⁰

Dicarbonyltriphenylphosphine-1-benzyl-2-methyl- π -allylcobalt from Chloro-1-benzyl-2-methyl- π -allylpalladium Dimer. A mixture of 1.15 g (2 mmole) of chloro-1-benzyl-2-methyl- π -allylpalladium dimer^{2,11} and 72 ml of 0.07 M $\text{NaCo}(\text{CO})_4$ in ether⁹ was stirred at room temperature under nitrogen for 1 hr. To the mixture was added 4.1 ml of 1.0 M triphenylphosphine in ether. After stirring at room temperature for 1 hr, the solvent was removed under reduced pressure and the crude product was purified by two recrystal-

(5) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3381 (1963).

(6) R. F. Heck, *ibid.*, **86**, 2819 (1964).

(7) R. F. Heck, *ibid.*, **87**, 4727 (1965).

(8) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

(9) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

(10) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

(11) This compound was prepared by stirring 0.62 g of phenylmercuric chloride, 4 ml of isoprene, and 20 ml of 0.1 M LiPdCl_3 in acetonitrile at room temperature overnight. The resulting solution was poured onto an alumina column, and the yellow product was eluted with methylene chloride. Recrystallization from ether-pentane gave a 48% yield of the product as yellow crystals, mp 158.5–159.5°.

lizations from ether by cooling in Dry Ice. There was obtained 0.86 g (41%) of yellow prisms, mp 104–105° dec, γ_{CO} , 1920, 1985, 2055 (vw) cm^{-1} in chloroform.

Anal. Calcd for $\text{C}_{31}\text{H}_{28}\text{O}_2\text{PCo}$: C, 71.26; H, 5.40. Found: C, 71.63; H, 5.72.

The nmr spectrum of the product in DCCl_3 was rather poorly resolved, probably because of paramagnetic impurities. Bands were observed at 60 Mc at -439 (aromatic protons), -191 (methylene group next to phenyl group), and -100 cps (methyl group), with smaller peaks also visible from the π -allylic hydrogens.

Dicarbonyltriphenylphosphine-1-acetyl-2-methyl- π -allylcobalt from Chloro-1-acetyl-2-methyl- π -allylpalladium Dimer. A mixture of 0.48 g (1 mmole) of chloro-1-acetyl-2-methyl- π -allylpalladium dimer⁴ and 35 ml of 0.07 *M* $\text{NaCo}(\text{CO})_4$ in ether⁹ was stirred under nitrogen at room temperature for 1 hr. The black precipitate of palladium metal was removed by centrifuging, and the clear, orange solution (26 ml) was transferred by means of a hypodermic syringe to a carbon monoxide filled gasometric apparatus thermostated at 0°. To the solution was added 2.5 ml of 1.0 *M* triphenylphosphine in ether at 0°. In 45 min 33 ml of gas was evolved. A calculation of the rate constant for the reaction gave as an average value for 10 points over about 5 half-lives $3.15 \pm 0.09 \times 10^{-3} \text{ sec}^{-1}$. This value is about what would have been expected on the basis of values obtained for related compounds.¹² Evaporation of the solvent in the reaction mixture under reduced pressure and two recrystallizations of the crude product from methylene chloride by adding pentane, at -80° under nitrogen, gave 0.33 g (35%) of orange crystals of the product. The complex was rather unstable at room temperature and oxidized in air. The material, mp 153–155° dec, had infrared bands in chloroform solution at 1650, 1945, 2000, and 2070 cm^{-1} .

Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3\text{PCo}$: C, 65.83; H, 5.10. Found: C, 66.58; H, 5.60.

Tetracarbonylcobaltotriphenylphosphine-1,1,2-trimethyl- π -allylpalladium. A mixture of 0.63 g (1.5 mmoles) of chloro-1,1,2-trimethyl- π -allylpalladium dimer³ and 45 ml of 0.07 *M* $\text{NaCo}(\text{CO})_4$ in ether⁹ was stirred under nitrogen at room temperature for 2 hr. Then 3.5 ml of 1.0 *M* triphenylphosphine in ether was added, and stirring was continued for another hour. The solvent was removed

under reduced pressure, and the product was extracted from the residue with methylene chloride. The methylene chloride extracts were concentrated to a few milliliters and diluted with several volumes of pentane. Cooling in Dry Ice produced red-brown crystals of the product. Another recrystallization in the same manner gave 0.12 g (6.5%) of product, mp 117–120° dec, with infrared carbonyl absorptions in chloroform at 1875, 1910, 1950, and 2025 cm^{-1} .

Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{O}_4\text{PCoPd}$: C, 53.99; H, 4.21; P, 4.97. Found: C, 53.98; H, 4.35; P, 4.27.

Chloro- π -allylpalladium Dimer from Tricarbonyl- π -allylcobalt. To a solution of 60 ml of 0.07 *M* $\text{NaCo}(\text{CO})_4$ in ether⁹ was added 4.5 ml of 1.0 *M* allyl chloride in ether under nitrogen. The solution was stirred at room temperature overnight. The solvent was then removed under reduced pressure at 0°, and the remaining tricarbonyl- π -allylcobalt was redissolved in 20 ml of acetonitrile at 0°. Thirty milliliters of 0.1 *M* LiPdCl_3 in acetonitrile¹³ was added, and the mixture was stirred at room temperature overnight. The entire solution was poured onto a column of alumina and chromatographed. The yellow product was eluted with 1% methanol in methylene chloride. Evaporation of the solvent under reduced pressure and recrystallization from methylene chloride-pentane gave 0.166 g (22%) of yellow prisms, mp 152–155° dec (lit.¹⁴ 145° dec).

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{Cl}_2\text{Pd}_2$: C, 19.70; H, 2.76; Cl, 19.38. Found: C, 19.82; H, 2.86; Cl, 20.16.

Chloro-1,3-dimethyl- π -allylpalladium Dimer from Tricarbonyl-1,3-dimethyl- π -allylcobalt. This reaction was carried out as in the preceding example using 2-chloro-3-pentene in place of allyl chloride. There was obtained after purification by chromatography and recrystallization from methylene chloride by adding pentane, 0.13 g (16%) of yellow plates, mp 186–190° dec.

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{Cl}_2\text{Pd}_2$: C, 28.46; H, 4.30. Found: C, 29.16; H, 4.79.

Another recrystallization from ethanol raised the melting point to 195–198° dec. The nmr spectrum of this product in deuteriochloroform at 60 Mc showed bands at -77.5 (doublet, $J_{\text{ab}} = 6.5$ cps with relative area of 6), -221 (pair of quartets of relative area 2 with $J_{\text{bc}} = 11$ cps), and -312 cps (a triplet with relative area 1).

(13) Only 1 mole of LiCl dissolves per mole of PdCl_2 in acetonitrile solution. Presumably $\text{LiPdCl}_3\text{CH}_3\text{CN}$ is formed.

(14) J. Smidt and W. Hafner, *Angew. Chem.*, 71, 284 (1959).

(12) R. F. Heck, *J. Am. Chem. Soc.*, 85, 655 (1963).

Nucleophilic Reactivity Constants toward Methyl Iodide and *trans*- $[\text{Pt}(\text{py})_2\text{Cl}_2]$

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois. Received August 11, 1967

Abstract: The rates of reaction of a number of nucleophiles with methyl iodide and *trans*- $[\text{Pt}(\text{py})_2\text{Cl}_2]$ have been measured in methyl alcohol at 25°. Relative nucleophilic reactivity parameters, $n_{\text{CH}_3\text{I}}$ and n_{Pt} , have been calculated. It was not found possible to correlate these numbers with each other or with other extra-kinetic data. Equations in the literature for predicting nucleophilic reactivity have only a limited range of usefulness.

The subject of nucleophilic reactivity continues to be of great interest. A number of recent reviews and discussions have appeared.³ There are also several semiempirical equations which attempt to predict and

correlate rate data of reactions presumed to occur by bimolecular nucleophilic displacement ($\text{S}_{\text{N}}2$) mechanisms.⁴ In particular, it has been of interest to try to relate rate constants to extra-kinetic properties such as redox potentials.⁵

A practical difficulty has been the lack of extensive data for a large number of nucleophiles reacting with

(1) Predoctoral fellow, National Institutes of Health, 1966–1968.
(2) Supported by the Royal Norwegian Council for Scientific and Industrial Research.

(3) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, 84, 16 (1962); R. F. Hudson, *Chimia* (Aarau), 16, 173 (1962); J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 14, 271 (1963); J. Miller, *J. Am. Chem. Soc.*, 85, 1628 (1963).

(4) These equations are reviewed by K. M. Ibne-Rasa, *J. Chem. Educ.*, 44, 89 (1967).

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