2-(Phenylazo)phenyl Complexes of the Transition Metals

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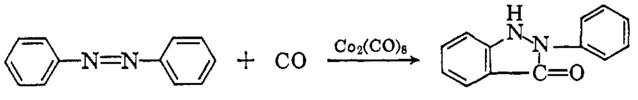
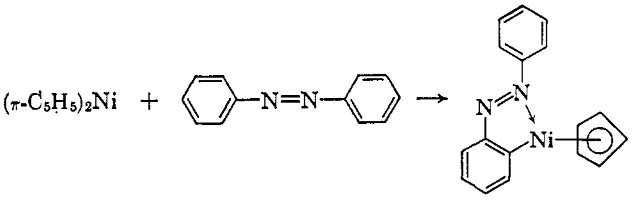
Contribution from the Research Center, Hercules Incorporated, Wilmington, Delaware 19899. *Received July 13, 1967*

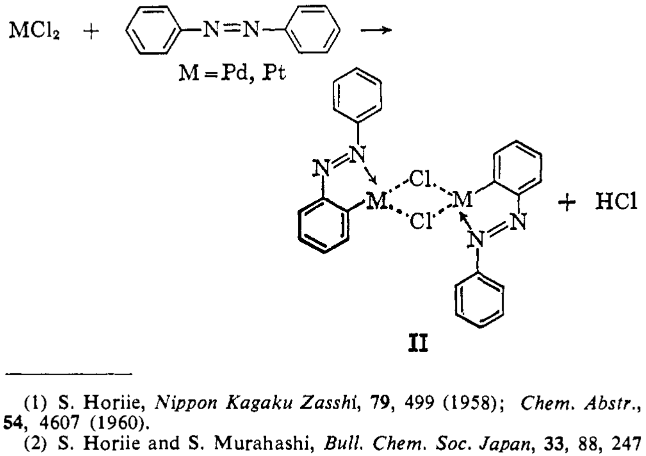
Abstract: 2-(Phenylazo)phenylmetal derivatives of cobalt, manganese, and rhenium have been prepared by a ligand-exchange reaction of the metal carbonyl anions with chloro-2-(phenylazo)phenylpalladium dimers.

The carbonylation of azobenzene catalyzed by octacarbonyldicobalt to form 2-phenyl-1H-indazolone has been studied by Horiie.[1,2] The reaction has been thought to proceed by way of cobalt–nitrogen-bonded intermediates which insert carbon monoxide and then cyclize by reacting with an aromatic hydrogen.[2-4] Two recent publications now raise a question as to whether another mechanism involving metalation of the *ortho* position of the benzene ring in azobenzene might be the correct mechanism. In 1963, Kleiman and Dubeck reported that bis(cyclopentadienyl)nickel reacted with azobenzene to produce π-cyclopentadienyl-2-(phenylazo)phenylnickel (I) as a surprisingly stable product.[5] In 1965, Cope and Siekman reported that apparently similar derivatives were obtained by allowing palladium or platinium chloride to react with azobenzene, the product being a chloro-2-(phenylazo)phenylmetal dimer (II).[6] Which of the two nitrogen atoms or if both are involved in bonding to the metal is not clear from the evidence obtained. Since *ortho* metalation by palladium also occurs with N,N-dimethylbenzylamine[7] and presumably not with N,N-dimethylaniline, coordination probably involves the nitrogen farthest from the metal.[8]





I



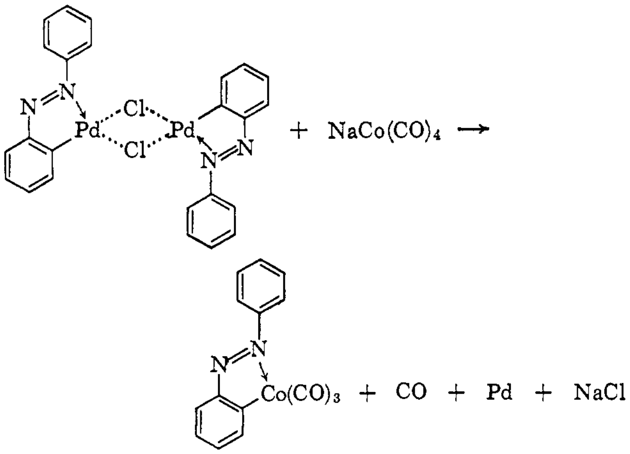
II

The present paper describes preparations of other 2-(phenylazo)phenylmetal derivatives and a preliminary investigation of the reactions of some of these compounds.

Results

The obvious route to other 2-(phenylazo)phenylmetal derivatives is by heating various metal compounds with azobenzene as was done to prepare the above-mentioned complexes. Unfortunately, this does not produce the same type of product when pentacarbonyliron is treated with azobenzene.[9] An attempt to produce tricarbonyl-2-(phenylazo)phenylcobalt (III) by heating octacarbonyldicobalt with azobenzene was also unsuccessful. A general method for the preparation of 2-(phenylazo)-phenylmetal derivatives was found, however, in the ligand-exchange reaction of the known chloro-2-(phenylazo)phenylpalladium dimer[6] with various metal carbonyl anions.

Tricarbonyl-2-(phenylazo)phenylcobalt (III) was obtained in 26% yield from the reaction of sodium tetracarbonylcobaltate with chloro-2-(phenylazo)phenylpalladium dimer. The cobalt complex is an orange



III

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[1] S. Horiie, *Nippon Kagaku Zasshi*, **79**, 499 (1958); *Chem. Abstr.*, **54**, 4607 (1960).

[2] S. Horiie and S. Murahashi, *Bull. Chem. Soc. Japan*, **33**, 88, 247 (1960).

[3] H. W. Sternberg and I. Wender, Special Publication No. 13, The Chemical Society, London, 1959, p. 35.

[4] R. F. Heck, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 204.

[5] J. P. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963).

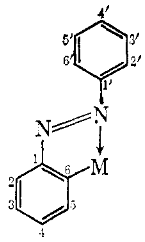
[6] A. C. Cope and R. W. Siekman, *ibid.*, **87**, 3273 (1965).

[7] A. C. Cope, J. M. Kliegman, and E. C. Friedrich, *ibid.*, **89**, 287 (1967).

[8] A related iron complex, dicarbonyldi[2-(4-tolylazo)-5-methylphenyl]iron has also been obtained from nonacarbonylidiiron and *p*-azotoluene.[9]

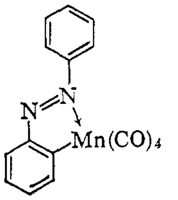
[9] M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Commun*, 543 (1965).

Table I. 2-(Phenylazo)phenylmetal Complexes



Compound				Found, %			Calcd, %		
Substituents	M	Mp, °C	ν_{CO}, cm^{-1}	C	H	N	C	H	N
H-	$Co(CO)_3$	64.0–64.5	2005, 2025, 2075	54.99	3.19	9.02	55.57	2.80	8.64
3,3′-$(CH_3)_2$-	$Co(CO)_3$	40.5–41.0	2005, 2025, 2075	57.94	4.09	8.02	57.97	3.72	7.96
4,4′-$(C_2H_5O)_2$-	$Co(CO)_3$	115.5–116.0	1995, 2015, 2070	55.82	4.56	7.20	55.35	4.16	6.80
4,4′-$(C_2H_5O)_2$-	$Co(CO)_2P(C_6H_5)_3$	178.5–179.5	1965, 2020	67.34	5.68	4.38	66.87	4.99	4.33
3′-CH_3O-	$Co(CO)_3$	31.0–31.5	2000, 2025, 2070	53.94	3.59	8.05	54.25	3.13	7.91
3′,4′,4,5-Dibenzo-	$Co(CO)_3$	144–145	2000, 2010 2065	65.59	3.54	6.78	65.11	3.09	6.60
H	$Mn(CO)_4$	112.5–113.0	1955, 2005, 2080	55.90	2.90	7.99	55.19	2.60	8.05
3′,4′,4,5-Dibenzo-	$Mn(CO)_4$	172.0–173.0	1955, 1995, 2005, 2085	64.41	3.22	6.55	64.30	2.92	6.25
H	$Re(CO)_4$	128.5–129.0	1945, 1995, 2095	40.13	2.10	5.88	40.08	1.89	5.84
4,4′-$(C_2H_5O)_2$-	$Re(CO)_4$	120.0–121.0	1945, 1955, 2005, 2095	42.61	3.19	5.12	42.32	3.02	4.94
H	$PdC_5H_7O_2$	182.5–183.5	. . .	53.15	4.40	7.36	52.80	4.14	7.25
H	PdC_5H_5	147.0–147.5	. . .	57.90	4.38	7.80	57.89	4.00	7.94

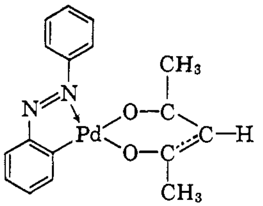
crystalline solid, mp 64°, which is oxidized only slowly by air. Tetracarbonyl-2-(phenylazo)phenylmanganese (IV) and tetracarbonyl-2-(phenylazo)phenylrhenium were obtained in a similar manner from sodium pentacarbonylmanganate and sodium pentacarbonylrhenate. These materials were also orange crystalline solids which were moderately stable in air.



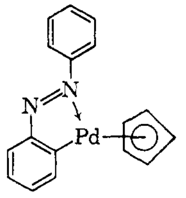
IV

Several substituted carbonyl-2-(phenylazo)phenylmetal derivatives were prepared by the above method from appropriately substituted chloro-2-(phenylazo)phenylpalladium dimers. The palladium compounds were all readily obtained by the method of Cope[6] by boiling the azoaromatic compound and lithium tetrachloropalladate in methanol. The new compounds prepared are listed in Table I. Attempts were made to form 2-(phenylazo)phenyliron complexes from sodium dicarbonylcyclopentadienyliron, from sodium tricarbonylnitrosylferrate, and from disodium tetracarbonylferrate. Reactions occurred, but pure products could not be isolated from the reaction mixtures.

The unusual stability of the carbon–metal σ bond in these 2-(phenylazo)phenylmetal complexes is shown by their unexpectedly high thermal stability and chemical behavior. Cope has shown that the palladium complex does not lose the 2-(phenylazo)phenyl group even on reaction with potassium cyanide.[6] We find also that acetylacetone replaces chloride rather than the 2-(phenylazo)phenyl group on reaction with II, forming V.



V



VI

Cyclopentadienylsodium reacts with I to form cyclopentadienyl-2-(phenylazo)phenylpalladium (VI) as an intensely purple, air-stable, sublimable solid, similar in properties to the corresponding nickel compound (I).

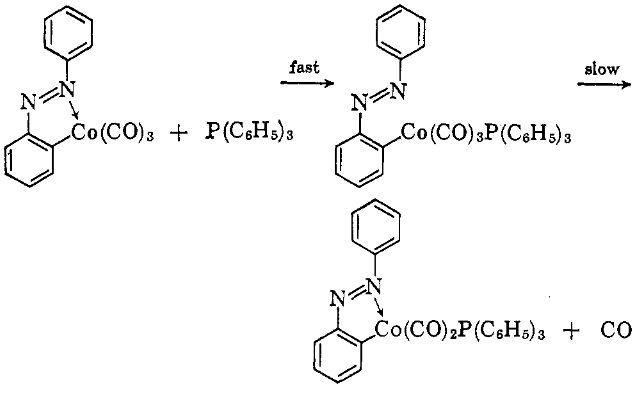
Tricarbonyl-2-(phenylazo)phenylcobalt (III) and its derivatives react readily with triphenylphosphine to form monotriphenylphosphine derivatives with loss of 1 mole of carbon monoxide. These complexes have proved to be rather difficult to isolate as pure substances probably because of instability as a result of there being too many large groups around the cobalt atom. The diethoxy derivative was isolated in a reasonably pure form.

A brief investigation of the reaction kinetics of some of the tricarbonyl-2-(phenylazo)phenylcobalt derivatives with triphenylphosphine was made in order to compare the reactivity of these materials with other cobalt carbonyl derivatives.[10] The reaction rates were measured by observing the rate of carbon monoxide evolution. The data obtained are given in Table II. The rates are proportional to the concentration of a 1:1 complex between the cobalt compound and the triphenylphosphine, suggesting that the coordinated azo nitrogen is rapidly replaced on cobalt by the phosphine with the resulting complex undergoing a slow, rate-determining loss of carbon monoxide.

Table II. Rates of Reaction of Tricarbonyl-2-(phenylazo)phenylcobalt and Some of Its Derivatives with Triphenylphosphine[a]

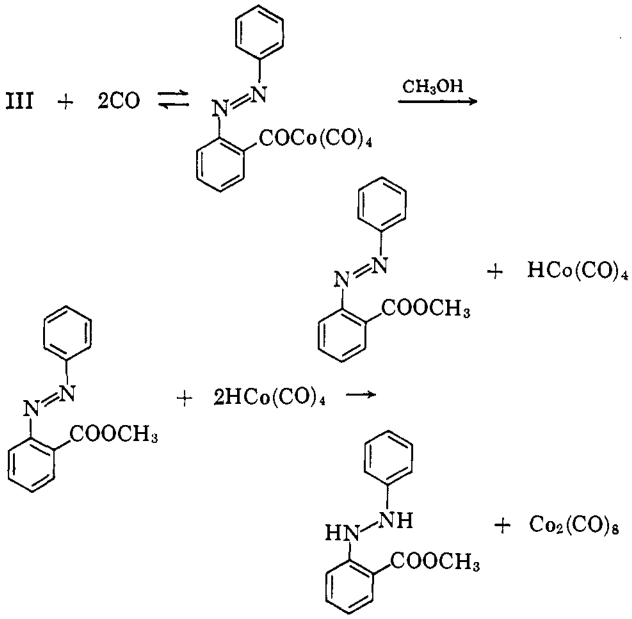
Deriv of III	Concn, *M*	Triphenylphosphine concn, *M*	Temp, °C	*k*, sec^{-1}
III	0.075	0.071	0	$(6.65–4.63) \times 10^{-4}$
	0.032	0.400	0	$1.22 \pm 0.01 \times 10^{-3}$
	0.097	0.400	0	$1.10 \pm 0.03 \times 10^{-3}$
	0.234	0.118	0	$1.49 \pm 0.09 \times 10^{-3}$
	0.098	0.667[b]	0	$1.81 \pm 0.01 \times 10^{-3}$
	0.039	0.400	25	$1.38 \pm 0.04 \times 10^{-2}$[c]
3,3′-$(CH_3)_2$–	0.082	0.400	0	$3.81 \pm 0.09 \times 10^{-3}$
4,4′-$(C_2H_5O)_2$–	0.061	0.429	0	$6.42 \pm 0.12 \times 10^{-4}$
3-NO_2–	0.038	0.375	0	$8.36 \pm 0.42 \times 10^{-4}$
3-CH_3O–	0.173	0.375	0	$1.13 \pm 0.06 \times 10^{-3}$

[a] Measured in ether solution. [b] Concentration of trimethyl phosphite. [c] $\Delta E^{\ddagger} = 15.7$ kcal, $\Delta S^{\ddagger} = 16.3$ eu.



At low concentrations of the cobalt complex and the triphenylphosphine, the first step becomes significant and a decreasing first-order rate is observed. Trimethyl phosphite reacts with III at a first-order rate different from triphenylphosphine as expected by the above mechanism. Substituent effects on the loss of carbon monoxide from the 1:1 complex show that a *m*-methyl group increases the rate by a factor of about 3 and a *p*-ethoxy group decreases the rate by one-half over the unsubstituted compound. A mono-*m*-nitro derivative was slightly less reactive than III. On the basis of the slight effect upon the rate, the nitro group was probably not in the metalated aromatic ring. The product may have been a mixture because neither it nor its triphenylphosphine derivative could be crystallized. A mono-*m*-methoxy derivative of III also reacted at about the same rate as III and therefore was probably substituted, at least mainly, in the nonmetalated ring.

Cope reported that the palladium complex (II) reacts with carbon monoxide in aqueous solution to form 2-phenyl-1H-indazolone,[11] the same compound that was obtained by Horiie by the cobalt-catalyzed carbonylation of azobenzene.[1,2] Surprisingly, the carbonylation of tricarbonyl-2-(phenylazo)phenylcobalt in methanol solution produced 2-carbomethoxyhydrazobenzene, presumably by the following mechanism.



We have found in methanol solution under similar conditions that chloro-2-(phenylazo)phenylpalladium dimer carbonylates to form 2-phenyl-1H-indazolone as the major product. These results, nevertheless, support the postulate that complex III is the intermediate in the cobalt carbonyl catalyzed carbonylation of azobenzene since the hydrazine derivative would form the indazole product under the conditions employed for the reaction. Apparently III is too reactive to be isolated from the direct reaction of octacarbonyldicobalt with azobenzene.

Thus, the above 2-(phenylazo)phenylmetal complexes appear to be members of a new class of stable σ-bonded transition metal–carbon compounds. It is not clear, however, why the presence of the 2-(phenylazo) group so profoundly affects the stability of the complexes and their ease of formation by direct metalation reactions.

Experimental Section

Chloro-2-(phenylazo)phenylpalladium Dimers. These compounds were all prepared by refluxing a 0.1 *M* solution of Li_2PdCl_4 in methanol with an equivalent amount of the appropriate azobenzene derivative for 1–3 hr. The red-to-brown solid products which precipitated during the reaction were filtered, washed with fresh methanol, and air-dried. The crude materials were used as they

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(10) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 657 (1963).

(11) A. C. Cope, Abstracts of the 19th National Organic Symposium, Tempe, Ariz., June 13–17, 1965, p 42.

were in most of the ligand-exchange reactions. The palladium compounds were so insoluble that they could be purified only by Soxhleting with methylene chloride. The products obtained in this way were nicely crystalline products, but some were still not analytically pure.

Chloro-2-(3-methylphenylazo)-4-methylphenylpalladium dimer formed small, dark red prisms, mp 276–277°.

Anal. Calcd for $C_{28}H_{26}N_4Cl_2Pd_2$: C, 47.89; H, 3.73; N, 7.98. Found: C, 48.34; H, 3.96; N, 8.09.

Chloro-2-(4-ethoxyphenylazo)-5-ethoxyphenylpalladium dimer formed small, brown crystals, mp 278.5–279.5°.

Anal. Calcd for $C_{32}H_{34}O_4N_4Cl_2Pd_2$: C, 46.73; H, 4.17; N, 6.82. Found: C, 46.52; H, 4.19; N, 6.51.

Chloro-2-(3-methoxyphenylazo)phenylpalladium dimer was obtained as a brown solid, mp 260–265° dec.

Anal. Calcd for $C_{26}H_{22}O_2N_4Cl_2Pd_2$: C, 44.22; H, 3.14; N, 7.94. Found: C, 44.80; H, 3.44; N, 6.93.

Tricarbonyl-2-(phenylazo)phenylcobalt. (1). An attempt to prepare this material by heating, in a closed bottle, a mixture of 3.24 g of $Co_2(CO)_8$ (10 mmoles) and 3.04 g of azobenzene (20 mmoles) under nitrogen in 10 ml of benzene containing 1 ml of dicyclohexylamine as a proton acceptor at 80° for 1 hr failed. The solution did not show the infrared carbonyl bands characteristic of the product. Longer heating, up to 20 hr, likewise failed. Evaporation of the solvent *in vacuo* at room temperature and extraction with a small volume of pentane, a known solvent for tricarbonyl-2-(phenylazo)phenylcobalt, also did not yield a detectable amount of the desired product.

(2). A mixture of 0.97 g (1.5 mmoles) of chloro-2-(phenylazo)phenylpalladium dimer and 45 ml of 0.07 *M* $NaCo(CO)_4$ in ether solution[12] was stirred magnetically under nitrogen for 30 min. The solvent was removed under reduced pressure at room temperature and the product extracted from the residue with pentane. The dark red extracts were centrifuged to separate insoluble material and concentrated at room temperature under reduced pressure to about 5 ml. On cooling in Dry Ice, orange plates separated. Another crystallization from pentane and one more from methanol gave 0.25 g (26%) of tricarbonyl-2-(phenylazo)phenylcobalt.

Tricarbonyl-2-(3-methylphenylazo)-4-methylphenylcobalt. This material was obtained as orange crystals in 26% yield also by the same procedure as was used in the preparation of tricarbonyl-2-(phenylazo)phenylcobalt above with chloro-2-(3-methylphenylazo)-4-methylphenylpalladium dimer.

Tricarbonyl-2-(4-ethoxyphenylazo)-5-ethoxyphenylcobalt. This compound was prepared from chloro-2-(4-ethoxyphenylazo)-5-ethoxyphenylpalladium dimer by the procedure used in the tricarbonyl-2-(phenylazo)phenylcobalt preparation above. A 26% yield of the product was obtained as yellow-orange needles from methanol solution.

Treatment of the product with excess triphenylphosphine in ether solution and evaporation of the solvent followed by recrystallization from CH_2Cl_2–ether gave a good yield of the monotriphenylphosphine derivative as dark red crystals.

Tricarbonyl-2-(3-methoxyphenylazo)phenylcobalt. This compound was obtained from chloro-2-(3-methoxyphenylazo)phenylpalladium dimer by the procedure used to prepare tricarbonyl-2-(phenylazo)phenylcobalt. The crude liquid product obtained gave very dark red crystals at −80° when dissolved in methanol. The material was recrystallized from methanol to give about a 3% yield of nearly black prisms of the product. The low yield of product obtained suggests that the palladium complex used may have been a mixture of isomers, although kinetic measurements made on the crude liquid product gave good first-order rate constants.

Tricarbonyl-2-(3-nitrophenylazo)phenylcobalt. This material was obtained as a dark red viscous liquid by the reaction of crude tricarbonyl-2-(3-nitrophenylazo)phenylcobalt with $NaCo(CO)_4$[12] as described above. The product could not be obtained in crystalline form, suggesting that it may have been a mixture of isomeric materials even though it gave a constant rate on reaction with triphenylphosphine. The triphenylphosphine derivative likewise could not be crystallized.

Tricarbonyl-2-(2-naphthylazo)naphthylcobalt. A mixture of 0.844 g (1 mmole) of chloro-2-(2-naphthylazo)naphthylpalladium dimer and 35 ml of 0.07 *M* $NaCo(CO)_4$ in ether[12] was stirred under nitrogen for 1 hr. The solvent was removed at room temperature under reduced pressure, and the product extracted from the residue with methylene chloride. The extracts were centrifuged to remove insoluble material, concentrated to a few milliliters, and about three or four times the volume of pentane was added. On cooling in Dry Ice, dark red crystals of the product were obtained. A second recrystallization in the same manner gave 0.28 g (33%) of pure product.

Tetracarbonyl-2-(phenylazo)phenylmanganese. A mixture of 0.644 g (1 mmole) of chloro-2-(phenylazo)phenylpalladium dimer, 10 ml of dry tetrahydrofuran, and 10 ml of 0.2 *M* $NaMn(CO)_5$ in tetrahydrofuran was stirred under nitrogen at room temperature for 1 hr. The solution was evaporated under reduced pressure and the product extracted from the residue with pentane. The extracts were centrifuged and concentrated to about 5 ml. On cooling in Dry Ice, dark red crystals of the product were obtained. Further purification by recrystallizing twice more from pentane gave 0.167 g (24%) of the product.

Tetracarbonyl-2-(2-naphthylazo)naphthylmanganese. A mixture of 0.633 g (1.5 mmoles) of chloro-2-(2-naphthylazo)naphthylpalladium dimer and 15 ml of 0.1 *M* $NaMn(CO)_5$ in tetrahydrofuran was stirred at room temperature under nitrogen for 1 hr. The solvent was then removed under reduced pressure at room temperature. The product was extracted from the residue with pentane. Cooling of the pentane solution in Dry Ice gave a mixture of red-brown needles and yellow prisms ($Mn_2(CO)_{10}$?), but on warming to room temperature the yellow compound redissolved leaving the red-brown compound relatively pure. The solid was separated and recrystallized from warm pentane by cooling to 0°. There was obtained 0.11 g (8%) of red-brown needles of tetracarbonyl-2-(2-naphthylazo)naphthylmanganese.

Tetracarbonyl-2-(phenylazo)phenylrhenium. A mixture of 0.64 g (1 mmole) of chloro-2-(phenylazo)phenylpalladium dimer, 10 ml of tetrahydrofuran, and 2.5 ml of 1 *M* $NaRe(CO)_5$ in tetrahydrofuran was stirred under nitrogen at room temperature overnight. The solvent was then evaporated at room temperature under reduced pressure. The product was extracted from the residue with pentane. Slow cooling of the concentrated extracts produced a mixture of colorless prisms ($Re_2(CO)_{10}$) and large red plates of the product which were easily separated by hand. Recrystallization of the red compound from methylene chloride by adding hexane gave about a 2% yield of the product as red plates.

Tetracarbonyl-2-(4-ethoxyphenylazo)-5-ethoxyphenylrhenium. A mixture of 1.22 g (1.5 mmoles) of chloro-2-(4-ethoxyphenylazo)-5-ethoxyphenylpalladium dimer, 6 ml of tetrahydrofuran, and 6 ml of 0.5 *M* $NaRe(CO)_5$ in tetrahydrofuran was stirred under nitrogen for 1 hr at 0° and for 1 hr at room temperature. The solvent was evaporated at room temperature under reduced pressure, and the residue was chromatographed on alumina. Some azophenetole was eluted first, and this was followed by the product. A recrystallization from pentane and two recrystallizations from absolute alcohol gave 0.20 g (12%) of yellow-brown prisms of the product.

Acetylacetonato-2-(phenylazo)phenylpalladium. A mixture of 0.644 g (1 mmole) of chloro-2-(phenylazo)phenylpalladium dimer, 8 ml of methanol, 0.135 g (2 mmoles) of sodium methoxide, and 2 ml of 2,4-pentanedione was stirred under nitrogen at room temperature overnight. The orange precipitate present was filtered, washed with methanol, and dried under reduced pressure. The solid was dissolved in methylene chloride and filtered from a little insoluble material, and the product was precipitated by adding pentane. There was obtained 0.30 g (39%) of orange-brown powder.

Cyclopentadienyl-2-(phenylazo)phenylpalladium. A mixture of 0.92 g (3 mmoles) of chloro-2-(phenylazo)phenylpalladium dimer, 15 ml of tetrahydrofuran, and 4.5 ml of 18% cyclopentadienylsodium in tetrahydrofuran (9 mmoles) was stirred under nitrogen at room temperature overnight. The solvent was evaporated under reduced pressure at room temperature. The residue was dissolved in methylene chloride and chromatographed on alumina. The purple-green eluate was concentrated to a few milliliters and hexane was added. On cooling to −5° dark purple-green crystals of the product were formed. Another recrystallization in the same manner gave 0.88 g (41.5%) of purified product.

Carbonylation of Tricarbonyl-2-(phenylazo)phenylcobalt. In a heavy-walled Pyrex bottle were placed a magnetic stirring bar and 1.29 g (2 mmoles) of chloro-2-(phenylazo)phenylpalladium dimer. The bottle was flushed with nitrogen, and 60 ml of 0.07 *M* $NaCo(CO)_4$ in ether[12] was added. The mixture was stirred at room temperature for 1 hr and the solvent removed under reduced pressure. The residue was treated with 30 ml of methanol. Insoluble material was removed by centrifuging, and the solution was transferred to a gasometric apparatus which was thermostated at 25° and filled

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

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 $C_{14}H_{14}N_3O_2$: 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 $C_{13}H_{10}N_2O$: 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 $C_{15}H_{14}ON_2$: 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

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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 anions[1] 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.

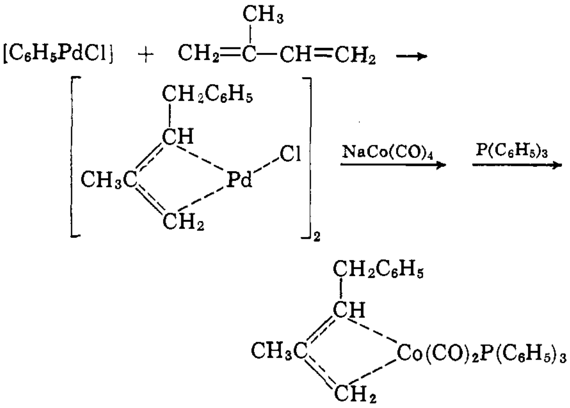
Results and Discussion

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.

$$0.5[\pi\text{-}C_3H_5PdCl]_2 + NaCo(CO)_4 \longrightarrow \pi\text{-}C_3H_5Co(CO)_3 + NaCl + CO + Pd$$

$$\pi\text{-}C_3H_5Co(CO)_3 + P(C_6H_5)_3 \longrightarrow \pi\text{-}C_3H_5Co(CO)_2P(C_6H_5)_3 + CO$$

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 $NaCo(CO)_4$ 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.



(1)

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

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

(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).