and selected bond angles are summarized in Table V.

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Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for **2a** (2 pages); a listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

Cobalt-Catalyzed Cyclocarbonylation of Acetylenes under Water Gas Shift Conditions: Selective Synthesis of Indan-1-ones

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Carbonylation of phenylacetylene derivatives by a cobalt catalyst under water gas shift conditions afforded 2-substituted indan-1-ones in satisfactory yields. Addition of phosphines enhanced both the activity and the selectivity of the catalyst. The deuterium-labeling studies showed that the migration of the ortho hydrogen of the phenyl group to the acetylenic carbon adjacent to the phenyl group took place in the cyclocarbonylation.

It is well-known that acetylenes undergo carbonylation to give various carbonylated products such as acrylic acid, acrylates, aldehydes, lactones, and cyclic ketones depending on the reaction conditions, including catalysts, additives, and hydrogen sources.[1] The C–H bond activation of aromatic compounds by transition metals is one of the current interests in organometallic chemistry and has been successfully applied to unique carbonylation reactions in organic syntheses.[2] The reaction of diphenylacetylene derivatives with $Fe_3(CO)_{12}$ has been reported to afford (1,1,1-tricarbonylferraindene)-π-tricarbonyliron complexes and tricarbonyl(2-phenylindenone)iron complexes.[3] Recently the stoichiometric reaction of diphenylacetylene with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ar$ has been reported to give cyclocarbonylated products, indenones, in good yields.[4]

The water gas shift reaction has recently been applied to unique organic syntheses such as selective hydrogenation and specific carbonylation.[5] We have previously reported a new method for the synthesis of furan-2(5*H*)-ones by carbonylation of acetylenes under water gas shift conditions.[6] This reaction was effectively catalyzed by rhodium carbonyl clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, but $Co_2(CO)_8$ was almost inactive for the formation of furan-2(5*H*)-ones. An addition of phosphines to the cobalt catalyst led to a different type of carbonylation, i.e., cyclocarbonylation of acetylenes, and we have reported the preliminary results in a previous paper.[7] We report herein in detail the cyclocarbonylation of phenylacetylene derivatives affording 2-substituted 1-indanones.

Results and Discussion

Reaction of Diphenylacetylene. Diphenylacetylene (**1a**) was reacted with water and carbon monoxide (100 atm) in the presence of a catalytic amount of $Co_2(CO)_8$ and triphenylphosphine in tetrahydrofuran at 220 °C. The

Table I. Effect of the Amount of Water for the Formation of Indanone 2a[a]

entry	amt of H_2O, mL (mmol)	convsn, %	selectivity,[b] %
1	4.0 (222)	100	69
2	1.0 (56)	100	73
3	0.5 (28)	99	69
4	0.2 (11)	100	75
5	0.1 (5.6)	91	55
6	0 (0)	42	5

[a] Diphenylacetylene, 5.0 mmol; $Co_2(CO)_8$, 0.125 mmol; Ph_3P, 0.25 mmol; THF, 40 mL; CO, 100 atm; reaction temperature, 220 °C; reaction time, 4 h. [b] Based on diphenylacetylene consumed (determined by GLC).

Table II. Effect of Phosphines Added[a]

entry	phosphine	P/Co	convsn, %	selectivity,[b] %
1			66	56
2	PPh_3	1/1	100	73
3	PPh_3	2/1	100	73
4	PPh_3	5/1	100	77
5	PPh_2Me	2/1	100	85
6	$PPhMe_2$	2/1	100	85
7	PBu_3	2/1	100	88

[a] Diphenylacetylene, 5.0 mmol; $Co_2(CO)_8$, 0.125 mmol; THF, 40 mL; H_2O, 56 mmol; CO, 100 atm; reaction temperature, 220 °C; reaction time, 4 h. [b] Based on diphenylacetylene consumed.

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[‡] Sekisui Chemical Co.

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Scheme I

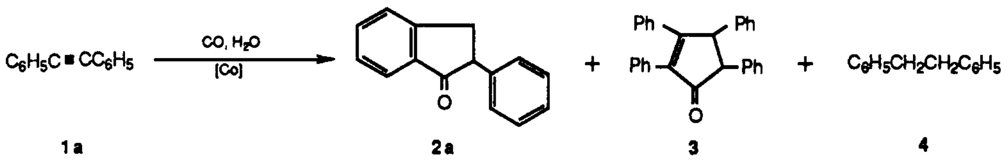

Table III. Effect of Solvent[a]

entry	catal, mol %	solvent, mL	convsn, %	selectivity,[b] %
1	2.5	THF, 40	100	73
2	2.5	DMF, 40	50	33
3	2.5	MeCN, 40	100	79
4	5.0	THF, 10	96	46
5	5.0	THF, 20	100	57
6	5.0	THF, 40	100	78
7[c]	5.0	THF, 40	100	82
8[c]	5.0	THF, 120	100	89

[a] Diphenylacetylene, 5.0 mmol; $PPh_3/Co_2(CO)_8$ ratio = 4; H_2O, 56 mmol; CO, 100 atm; reaction temperature, 220 °C; reaction time, 4 h. [b] Based on diphenylacetylene consumed. [c] Diphenylacetylene, 2.5 mmol.

products were isolated by column chromatography on silica. Recrystallization from ethanol gave 2-phenylindan-1-one (**2a**) in good yield (Scheme I). Tetraphenylcyclopentenone (**3**) and bibenzyl (**4**) were detected as the byproducts. The indanone (**2a**) thus obtained is derived from the cyclocarbonylation of **1a** with 1 molecule of carbon monoxide and 1 molecule of hydrogen via aromatic C–H bond activation. By use of D_2O instead of H_2O, the deuterated indanone was obtained, which indicates that hydrogen comes from water. Use of molecular hydrogen as the hydrogen source gave only bibenzyl in good yield. The presence of water is, therefore, essential to the formation of **2a**.

We have now investigated the reaction under various conditions using **1a** as a reactant. The effect of the amount of water used on the formation of **2a** is shown in Table I. In the presence of water more than 0.2 mL (11 mmol, H_2O/acetylene = 2.2), **2a** was obtained in satisfactory yield, although only a trace amount of **2a** was formed without water.

As shown in Table II, addition of phosphines to $Co_2(CO)_8$ catalyst enhanced both the activity and the selectivity of the catalyst. No appreciable change was observed when the ratio of P to Co was increased from 1:1 to 5:1. The dependence of the selectivity on the electronic properties of phosphines was also investigated. In this case, a trend was observed for the yield of **2a** as a function of the basicity of phosphines. Use of tri-*n*-butylphosphine especially gave the best result.

It is known that cobalt carbonyl reacts with phosphines to give the phosphine-substituted complexes, $[Co(CO)_3(PR_3)]_2$; thus, $[Co(CO)_3(PPh_3)]_2$ and $[Co(CO)_3(PBu_3)]_2$ may be expected to show the same activity as the two-component system, $Co_2(CO)_8/PR_3$. In fact, they showed high activities and gave **2a** with 100% conversion and 68% selectivity and with 100% conversion and 89% selectivity, respectively.

The solvent also has a noticeable influence on both the activity and the selectivity of the catalyst system, as shown in Table III. Tetrahydrofuran and acetonitrile gave good results, while the reaction proceeded with low conversion and poor selectivity in *N,N*-dimethylformamide. It should be noted that the selectivity for **2a** also depended upon the concentration of the reactants. At a low concentration of the reactants, the side reactions giving **3** and **4** were extremely depressed, and **2a** was obtained almost exclusively.

Table IV. Effect of Reaction Temperature[a]

entry	reaction temp, °C	convsn, %	selectivity,[b] %
1	200	89	32
2	220	100	73
3	240	100	76

[a] Diphenylacetylene, 5.0 mmol; $Co_2(CO)_8$, 0.125 mmol; PPh_3, 0.5 mmol; THF, 40 mL; CO, 100 atm; reaction time 4 h. [b] Based on diphenylacetylene consumed.

Table V. Effect of Pressure[a]

entry	init pressure of CO, atm	convsn, %	selectivity,[b] %
1	20	22	0[c]
2	50	99	77
3	100	100	73
4	200	100	79

[a] Diphenylacetylene, 5 mmol; $Co_2(CO)_8$, 0.125 mmol; PPh_3, 0.5 mmol; THF, 40 mL; reaction temperature, 220 °C; reaction time, 4 h. [b] Based on diphenylacetylene consumed. [c] Cobalt metals were deposited.

Table VI. Reactions of Various Acetylenes[a]

1	products 2	products 5	products 6	yield,[b] %	isomer ratio (2/5)
a: R = Ph, R′ = H	**a**			77	
b: R = Ph, R′ = Me-2	**b**	**b**		65	50/50[c]
c: R = Ph, R′ = Me-4	**c**	**c**		74	52/48[c]
d: R = Ph, R′ = OMe-4	**d**	**d**		86	
e: R = Ph, R′ = Cl-4	**e**	**e**		63	41/59
f: R = CH═CHPh(*E*), R′ = H			**f**	41	
g: R = Me, R′ = H			**g**	17[d]	

[a] Acetylene, 5.0 mmol; $[Co(CO)_3(PBu_3)]_2$, 0.125 mmol; H_2O, 56 mmol; CO, 100 atm; reaction temperature, 220 °C; 4 h. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] Determined by GLC.

As can be seen in Table IV, a reaction temperature of higher than 220 °C was required to achieve a high activity and a good selectivity of the catalytic system. A decrease of the reaction temperature to 200 °C lowered the conversion and the selectivity.

The effect of the pressure of carbon monoxide is shown in Table V. The reaction proceeded under 50 atm of initial pressure to give **2a** in good yield with a high selectivity. Increasing the initial pressure up to 200 atm, no appreciable change was observed in both the yield and the selectivity. Under 20 atm of initial carbon monoxide pressure, **2a** was not formed and cobalt metals were deposited via decomposition of the catalyst.

Reaction of Various Acetylenes. Unsymmetrically substituted acetylenes also afforded corresponding indanones as shown in Table VI. Diphenylacetylene derivatives bearing a substituent, R′, at the ortho or para position

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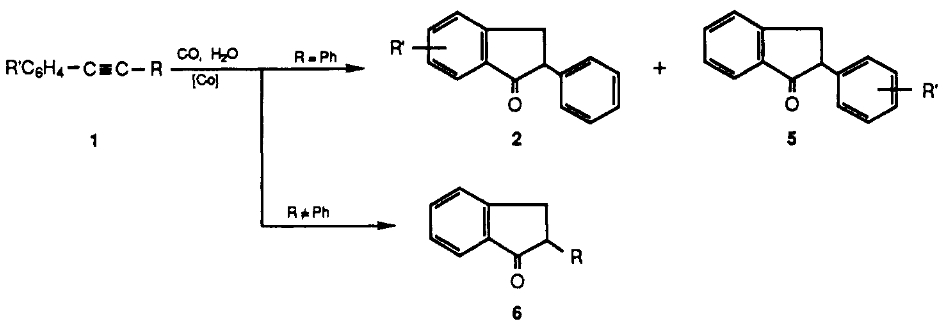
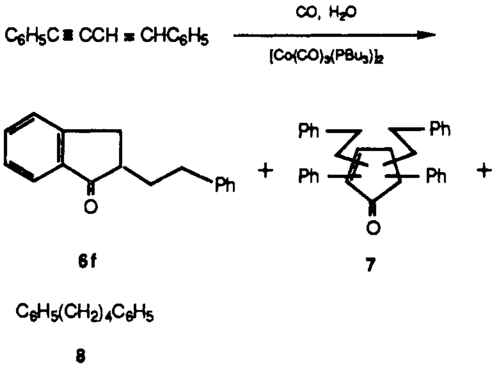
Scheme II[a]

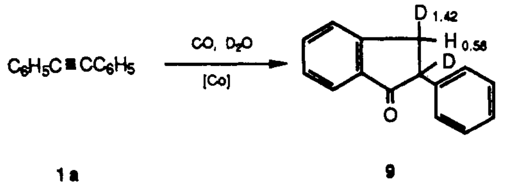


[a] Table entry letters define R and R'.

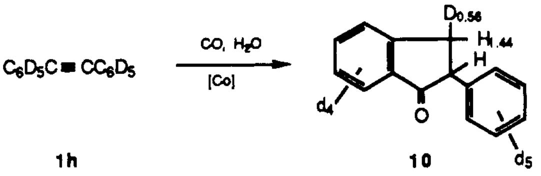
Scheme III



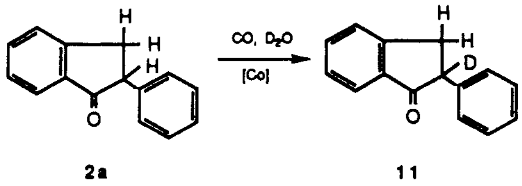
Scheme IV



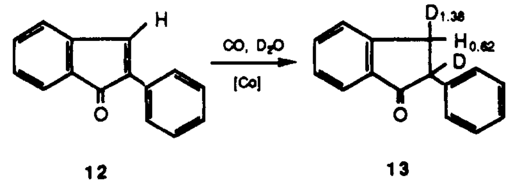
Scheme V



Scheme VI



Scheme VII



of one of the phenyl groups gave two structural isomers, **2b–e** and **5b–e** (Scheme II). It seems that the ratio is mainly affected by the electronic nature of the substituents, R', rather than the steric one, because the ortho-substituted diphenylacetylene derivative, **1b**, which has steric hindrance around the acetylenic bond, gave almost the same isomer ratio (about 1:1) as the para-substituted one, **1c**. (*p*-Chlorophenyl)phenylacetylene (**1e**) was cyclocarbonylated preferentially with the benzene ring having no chloro substituent, while the *p*-methyl-substituted one (**1c**) gave a 1:1 isomer ratio. This suggests that the ring formation to construct the indanone structure may proceed via an electrophilic substitution on the benzene ring. A conjugated enyne-like 1,4-diphenylbut-1-en-3-yne (**1f**) gave indanone derivative **6f** in moderate yield (Scheme III). Cyclopentenone derivative **7** and 1,4-diphenylbutane (**8**) were obtained as the byproducts. The present reaction may be applicable to alkyl-substituted acetylenes such as 1-phenylpropyne, though the yield was not as high. The hydrogenated products were major in these cases.

Deuterium-Labeling Experiment. The presence of water is essential for the formation of indanones from phenylacetylene derivatives as described in the preceding section. For the reaction path, it is supposed that indenone derivatives are formed at the first step through the cyclocarbonylation of phenylacetylene derivatives, followed by hydrogenation to afford indanones. Important information characterizing the reaction course may be obtained from the deuterium-isotope-labeling experiments.

By using D_2O instead of H_2O, **1a** gave the deuterated indanone **9** (Scheme IV). The 360-MHz ^1H NMR spectrum of **9** exhibited resonances in the aliphatic region, which shows that the hydrogen of the aromatic C–H bond migrated to the acetylenic carbon of diphenylacetylene during the cyclocarbonylation. Judging from the intergration of the ^1H NMR spectrum, the hydrogen/deuterium ratio of the methylene group of **9** was 0.58/1.42 and the methyne group was almost perfectly deuterized.

The reaction of decadeuteriodiphenylacetylene (**1h**) in the presence of H_2O was also carried out (Scheme V). The ^1H NMR spectrum of the resultant indanone, **10**, exhibited resonances only in the aliphatic region. Assuming that the methyne group of **10** was composed of hydrogen alone, the integration of methylene protons in the ^1H NMR spectrum showed that the deuterium/hydrogen ratio in the methylene group of **10** becomes 0.56/1.44. These experimental data reveal at least 56% of the hydrogens of the aromatic C–H bond migrated directly to the acetylenic carbon of diphenylacetylene during the cyclocarbonylation.

When the reaction of **2a** was run in the presence of D_2O in the same reaction conditions, the hydrogen of the methyne group of the indanone (**11**) produced was almost perfectly exchanged with deuterium, while the hydrogens of the methylene group were intact (Scheme VI).

Indenone **12** prepared by an alternative method, also gave the deuterated indanone **13** by the same treatment (Scheme VII). The ^1H NMR spectrum showed that the

Scheme VIII

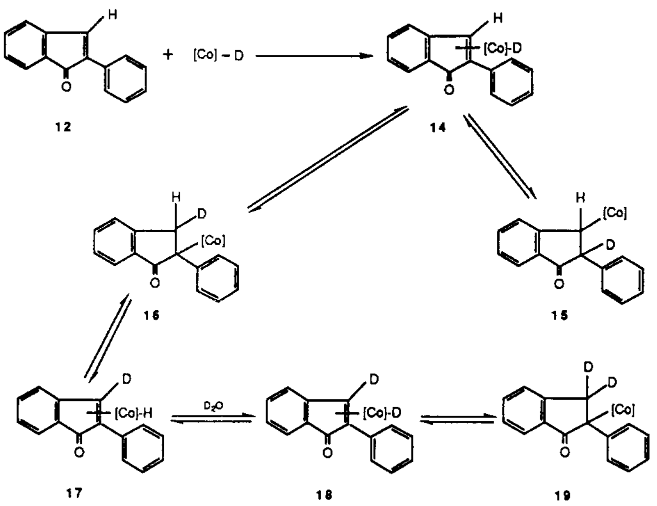
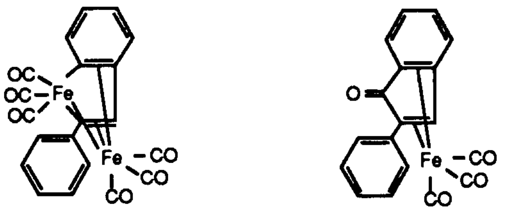
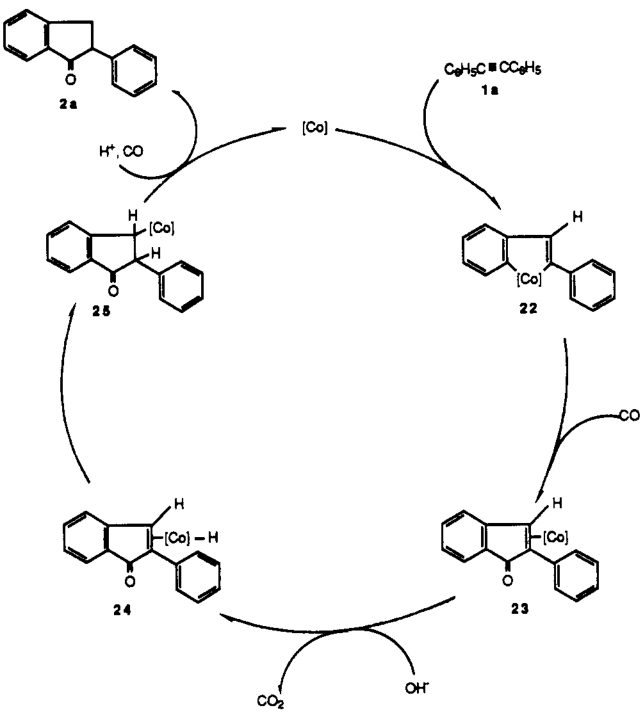


Chart I



20 21

Scheme IX



hydrogen/deuterium ratio in **13** was 0.62/1.38 and the hydrogen of the methyne group was also entirely exchanged by deuterium.

A decrease of the hydrogen/deuterium ratio of the methylene group of indanone should occur during the reduction of the C=C double bond of indenone under the water gas shift reaction conditions, because the hydrogen of the methylene group of indanone did not exchange with deuterium under the same reaction conditions. Exchange of hydrogen in the 3-position on indenone with deuturium may take place via a reversible insertion process of the C=C double bond to the [Co]-D bond, as illustrated in Scheme VIII.

Interestingly, the hydrogen/deuterium ratio of the methylene group of **9** is in good agreement with that of **13**. These data suggest strongly that the hydrogen of the aromatic C-H bond migrated directly without any exchange to produce **12** in the cyclocarbonylation of diphenylacetylene and the resultant **12** was hydrogenated subsequently under the water gas shift reaction conditions to afford **2a**.

Mechanism. It has been reported that $Fe_3(CO)_{12}$ reacts with diphenylacetylene (**1a**) to afford ferraindene complex **20**, which converts to (indenone)iron complex **21** by the reaction with carbon monoxide[3] (Chart I). Analogous types of intermediates would be involved in our catalytic cycle. A possible reaction pathway for the formation of indan-1-one is shown in Scheme IX. Coordination of diphenylacetylene (**1a**) to cobalt complex could induce an electrophilic attack of the central cobalt metal on the benzene ring and migration of the aromatic hydrogen to the acetylenic carbon to give cobaltaindene complex **22**. The formation of (indenone)cobalt complex **23** could proceed by replacement of the ring-bonded Co moiety in **22** by carbon monoxide. The resultant indenone could be hydrogenated by the [Co]-H species produced under water gas shift reaction conditions to yield indanone **2a** as discussed above.

Experimental Section

General Procedure. Melting points were recorded on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 295 infrared spectrophotometer. NMR spectra were recorded on a Bruker AM-360 or JEOL JNR-PMX 60SI. NMR spectra are expressed in parts per million from Me_4Si as internal standard. The mass spectra were obtained on a JEOL JMS 06. Gas chromatography was performed on a Shimazu GC-12A, using a helium carrier gas flow. The column used was a 5-m 5% Silicon OV-1. Elemental analyses were performed by Material Analysis Center, ISIR, Osaka University. $Co_2(CO)_8$[8] and $[Co(CO)_3(PR_3)]_2$[9] were prepared according to the reported procedures. Other chemicals were distilled or recrystallized before use. Solvents were purified by standard methods.

Reaction of Acetylenes under Water Gas Shift Conditions. 1. Reaction of Diphenylacetylene (1a). Into a 100-mL stainless steel autoclave was placed 40 mL of THF. Nitrogen gas was bubbled into the solvent and then 0.89 g (5.0 mmol) of **1a**, 132 mg (0.5 mmol) of triphenylphosphine, 1 mL (56 mmol) of H_2O, and 43 mg (0.125 mmol) of $Co_2(CO)_8$ were successively added. The reaction system was flushed three times with CO and then charged at room temperature to an initial CO pressure of 100 atm. The reaction was carried out at 220 °C for 4 h. It was observed by silica gel thin-layer chromatography (TLC) that the reaction proceeded with good selectivity. The reaction mixture was diluted with 50 mL of benzene and washed with water. Benzene solution was then dried over sodium sulfate. After removal of the solvent, the products were separated by silica gel column chromatography with 1:1 hexane-benzene as the eluent. **2a** (769 mg, 74%) was isolated as the main product. **3** (88 mg, 9%) and bibenzyl (**4**; 27 mg, 3%) were obtained as the byproducts.

2a: colorless columns from ethanol, mp 77-78 °C (lit. 77-77.5 °C[10]); ^1H NMR (360 MHz, $CDCl_3$) δ 3.27 (dd, 1 H, J = 4.0 Hz, J = 17.4 Hz, C*H*H), 3.69 (dd, 1 H, J = 8.3 Hz, J = 17.4 Hz, CH*H*), 3.89 (dd, 1 H, J = 8.3 Hz, J = 4.0 Hz, O=CCH), 7.17-7.34 (m, 5 H, Ph), 7.42, 7.53, 7.65, 7.81 (t, d, t, d, 4 H, arom); IR (Nujol) 1720 cm^{-1}; MS m/z 208 (M^+), 179, 178. Anal. Calcd for $C_{15}H_{12}O$:

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[9] Baillie, T. J.; Booth, B. L.; McAnliffe, C. A. *J. Organomet. Chem.* **1973**, *54*, 275. Piacenti, F.; Bianchi, M.; Bennedetti, E. *Chim. Ind. (Milan)* **1967**, *49*, 245.

[10] Hussey, A. S.; Herr, R. R. *J. Org. Chem.* **1959**, *24*, 843.

C, 86.51; H, 5.81. Found: C, 86.63; H, 5.56.

3: colorless prisms from ethanol, mp 155–160 °C (lit. 161–162 °C[11]); ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.7 (d, 1 H, *J* = 2 Hz, C=CCH), 4.5 (d, 1 H, *J* = 2 Hz, O=CCH), 7.1–7.5 (m, 20 H, arom); MS *m/z* 386 (M$^+$).

4: colorless columns from ethanol, mp 50–52 °C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 2.85 (s, 4 H, CH$_2$CH$_2$), 7.2 (s, 10 H, arom); MS *m/z* 182 (M$^+$).

2. **Reaction of (*o*-Tolyl)phenylacetylene (1b).** By the procedure for **1a** and with 86 mg (0.125 mmol) of [Co(CO)$_3$(PBu$_3$)]$_2$ instead of Co$_2$(CO)$_8$ and triphenylphosphine, 0.96 g (5.0 mmol) of **1b** was reacted to give, after purification by silica gel column chromatography, 720 mg (65%) of an isomeric mixture of **2b** and **5b**. The **2b**/**5b** ratio was found to be 50/50 from the integration of the ^{1}H NMR spectrum.

2b/**5b**: ^{1}H NMR (360 MHz, CDCl$_3$) δ 2.32 and 2.35 (s/s, 3 H/3 H, CH$_3$ for **2b**/**5b**, 3.05–3.15 (m, 1 H/1 H, C*H*H for **2b**/**5b**), 3.54 and 3.65 (q/q, 1 H/1 H, *J* = 8.3 and 17.8 Hz/*J* = 8.3 and 17.3 Hz, CH*H* for **2b**/**5b**), 3.85 and 4.07 (q/q, 1 H/1 H, *J* = 8.3 and 4.4 Hz/*J* = 8.3 and 4.3 Hz, O=CCH for **2b**/**5b**), 6.9–7.7 (m, 8 H/7 H, arom for **2b**/**5b**), 7.81 (d, 1 H, *J* = 7.5 Hz, *o*-H to C=O for **5b**).

3. **Reaction of (*p*-Tolyl)phenylacetylene (1c).** By the procedure described for **1b**, 0.98 g (5.0 mmol) of **1c** was reacted to give, after purification by silica gel column chromatography, 810 mg (74%) of the product mixture (**2c**/**5c**). The isomeric ratio of **2c** and **5c** was found to be about 52/48.

2c/**5c**: ^{1}H NMR (360 MHz, CDCl$_3$) δ 2.31 (s, 3 H, CH$_3$ for **2c**), 2.42 (s, 3 H, CH$_3$ for **5c**), 3.2–4.0 (m/m, 3 H/3 H, CH$_2$CH for **2c**/**5c**), 7.0–7.7 (m/m, 8 H/7 H, arom from **2c**/**5c**), 7.80 (d, 1 H, *J* = 7.5 Hz, *o*-H to C=O for **5c**).

4. **Reaction of (4-Methoxyphenyl)phenylacetylene (1d).** By the procedure for **1b**, 1.04 g (5.0 mmol) of **1d** was reacted to give, after purification by silica gel column chromatography, 1.03 g (87%) of the products (**2d**/**5d**).

2d/**5d**: ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.1–3.3 (m/m, 1 H/1 H, C*H*H for **2d**/**5d**), 3.6–4.0 (m/m, 5 H/5 H, C*H*CH*H* and CH$_3$ for **2d**/**5d**), 6.8–7.8 (m/m, 8 H/8 H, arom for **2d**/**5d**).

5. **Reaction of (4-Chlorophenyl)phenylacetylene (1e).** By the procedure for **1b**, 1.06 g (5.0 mmol) of **1e** was reacted to give, after purification by silica gel column chromatography, 318 mg (26%) of **2e** and 443 mg (37%) of **5e**.

2e: pale-yellow crystals, mp 89–91 °C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.0–3.9 (m, 3 H, aliph), 7.5 (s, 5 H, Ph), 7.3–7.9 (m, 3 H, arom); IR (Nujol) 1730 cm^{-1}.

5e: colorless fine needles, mp 86–87 °C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.0–3.9 (m, 3 H, aliph), 7.0–8.0 (m, 8 H, arom); IR (Nujol) 1730 cm^{-1}.

6. **Reaction of 1,4-Diphenylbut-1-en-3-yne (1f).** By the procedure for **1b**, 1.02 g (5.0 mmol) of **1f** was reacted to give, after purification by silica gel column chromatography, 485 mg (41%) of **6f**, 210 mg (19%) of **7**, and 163 mg (16%) of **8**.

6f: pale-yellow oil; ^{1}H NMR (60 MHz, CDCl$_3$) δ 1.5–3.5 (m, 7 H, aliph), 7.2–7.9 (m, 9 H, arom); IR (neat) 1720 cm^{-1}; MS *m/z* 236 (M$^+$).

7: pale-yellow oil; ^{1}H NMR (60 MHz, CDCl$_3$) δ 1.5–3.5 (m, 10 H, aliph), 7.0–8.0 (m, 20 H, arom); IR (neat) 1725 cm^{-1}; MS *m/z* 442 (M$^+$).

8: colorless oil; ^{1}H NMR (60 MHz, CDCl$_3$) δ 1.6 (m, 4 H, CH$_2$C*H*$_2$CH$_2$C*H*$_2$), 2.6 (m, 4 H, PhC*H*$_2$), 7.2 (s, 10 H, arom).

7. **Reaction of 1-Phenylpropyne (1g).** By the procedure for **1b**, 590 mg (5.09 mmol) of **1g** was reacted. Gas chromatographic analysis of the solution showed the formation of **6g** in 17% yield and 1-phenylpropane in 39% yield. The usual workup gave **6g** as a colorless oil, which was purified by preparative TLC (silica gel, dichloromethane).

6g: ^{1}H NMR (360 MHz, CDCl$_3$) δ 1.32 (d, 3 H, *J* = 7.0 Hz, CH$_3$), 2.73 (m, 2 H, CH$_2$), 3.40 (m, 1 H, CH$_3$C*H*), 7.3–7.8 (m, 4 H, arom) (lit. δ 1.30 (d, 3 H), 2.70 (m, 2 H), 3.40 (m, 1 H), 7.3–7.8 (4 H, arom)[12]); IR (Nujol) 1720 cm^{-1}; MS *m/z* 146 (M$^+$).

Deuterium-Labeling Experiment. 1. Reaction of 1a in the Presence of D$_2$O. In a 100-mL stainless steel autoclave, 0.45 g (2.5 mmol) of **1a**, 43 mg (0.0625 mmol) of [Co(CO)$_3$(PBu$_3$)]$_2$, 20 mL of freshly distilled THF, and 5 mL (250 mmol) of D$_2$O were placed. The reaction systems was flushed three times with CO and then charged at room temperature to an initial CO pressure of 100 atm. The reaction was carried out at 220 °C for 4 h. After purification by silica gel column chromatography, 341 mg (65%) of deuterated indanone (**9**) was isolated.

9: colorless crystals from hexane–benzene, mp 76–78 °C; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.23 and 3.65 (br s, br s, 0.57 H, CHH), 7.17–7.34 (m, 5 H, Ph), 7.42, 7.53, 7.65, 7.81 (t, d, t, d, 4 H, arom); MS *m/z* 211, 210, 209.

2. **Preparation of Decadeuteriodiphenylacetylene (1h).** A solution of 3.8 g (15 mmol) of iodine in 15 mL of hexadeuteriobenzene was stirred at 40 °C for 30 min in an atmosphere of nitrogen and then 4.4 g (33 mmol) of anhydrous copper(II) chloride and 4.4 g (33 mmol) of well-pulverized aluminium chloride were added with stirring. After the stirring was continued for 2 h, the solution was poured over ice in a beaker. The organic layer was extracted with ether and washed sequentially with diluted aqueous sodium bicarbonate and water and then dried over anhydrous sodium sulfate. Evaporation of ether and hexadeuteriobenzene gave the crude oily product that was purified by distillation to yield 4.5 g (73%) of pentadeuteriophenyl iodide: bp 67–68 °C (15–16 mmHg).

To a solution of 4.5 g (21.7 mmol) of pentadeuteriophenyl iodide in 60 mL of diethylamine maintained under nitrogen atmosphere was added subsequently 70 mg (0.1 mmol) of dichlorobis(triphenylphosphine)palladium and 38 mg (0.2 mmol) of copper(I) chloride. Then acetylene gas was bubbled through the solution at room temperature for 5 h, and the solution was refluxed for 1 h. After removal of salts by filtration and evaporation of the solvent, a crude crystalline product was found. Purification by silica gel chromatography gave 1.75 g (86%) of decadeuteriodiphenylacetylene (**1h**).

1h: mp 63–64 °C; MS *m/z* 188 (M$^+$).

3. **Reaction of 1h in the Presence of H$_2$O.** By analogy with the same procedure as for **1a** and with 35 mg (0.5 mmol) of [Co(CO)$_3$(PBu$_3$)]$_2$, 20 mL of freshly distilled THF, and 0.5 mL (28 mmol) of H$_2$O, 377 mg (2.0 mmol) of **1h** was reacted to give, after purification by silica gel column chromatography, 248 mg (57%) of deuterated indanone (**10**).

10: colorless crystals from hexane–benzene; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.28 and 3.70 (q, q, 1.44 H, CHH), 3.90 (q, 1 H, O=CCH); MS *m/z* 218, 217, 216.

4. **Reaction of Indanone (2a) in the Presence of D$_2$O.** By the procedure described for **1a** and with 17 mg (0.025 mmol) of [Co(CO)$_3$(PBu$_3$)]$_2$, 10 mL of THF, and 0.2 mL (10.0 mmol) of D$_2$O, 208 mg (1.0 mmol) of **2a** was reacted to yield, after purification by silica gel column chromatography, 194 mg (93%) of deuterated indanone (**11**).

11: colorless crystals from hexane–benzene; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.24 (d, 1 H, *J* = 17.4 Hz, C*H*H), 3.66 (d, 1 H, *J* = 17.4 Hz, CH*H*), 7.17–7.34 (m, 5 H, Ph), 7.42, 7.53, 7.65, 7.81 (t, d, t, d, 4 H, arom); MS *m/z* 210, 209, 208.

5. **Preparation of 2-Phenyliden-1-one (12).** To a solution of 1.57 g (7.5 mmol) of **2a** in 50 mL of ether maintained at 0 °C under an atmosphere of nitrogen was added a catalytic amount of aluminium chloride. Then 1.3 g (8 mmol) of bromine was added dropwise in about 5 min with stirring. After the solution was stirred for 10 min, evaporation of the solvent gave a crude crystalline product, which was washed with water and dried in a desiccator to yield 2.01 g (93%) of 2-bromo-2-phenylindan-1-one. To a solution of 1.0 g (3.5 mmol) of 2-bromo-2-phenylindan-1-one in benzene was added with stirring 0.53 g (3.5 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under nitrogen atmosphere at room temperature. After 30 min, the solution was filtered to remove the salts and evaporated to dryness. Subsequently purification by silica gel column chromatography gave 350 mg (49%) of **12**.

12: orange crystals, mp 94–97 °C; ^{1}H NMR (360 MHz, CDCl$_3$) δ 7.0–7.5 (m, 8 H, arom), 7.65 (s, 1 H, C=CH), 7.79 (d, 1 H, *J* = 7.1 Hz, *o*-H to C=O); IR (Nujol) 1720 cm^{-1}.

6. **Reaction of 12 in the Presence of D$_2$O.** By the procedure for **1a** and with 17 mg (0.025 mmol) of [Co(CO)$_3$(PBu$_3$)]$_2$, 10 mL of freshly distilled THF, and 2 mL (100 mmol) of D$_2$O, 206 mg (1.0 mmol) of **12** was reacted at 220 °C for 3.5 h to give, after

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purification by silica gel chromatography, 131 mg (63%) of deuterated indanone **13**.

13: colorless crystals from hexane–benzene; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.23 and 3.65 (br s, br s, 0.62 H, CHH), 7.17–7.34 (m, 5 H, Ph), 7.42, 7.53, 7.65, 7.81 (t, d, t, d, 4 H, arom); MS *m/z* 211, 210, 209.

Registry No. **1a**, 501-65-5; **1b**, 14309-60-5; **1c**, 3287-02-3; **1d**, 7380-78-1; **1e**, 5172-02-1; **1f**, 13343-79-8; **1g**, 673-32-5; **1h**, 19339-46-9; **2a**, 16619-12-8; **2b**, 117482-13-0; **2c**, 117482-15-2; **2d**, 108840-75-1; **2e**, 23909-34-4; **3**, 7317-52-4; **4**, 103-29-7; **5b**, 117482-14-1; **5c**, 784-75-8; **5d**, 1086-43-7; **5e**, 14087-87-7; **6f**, 117482-16-3; **6g**, 17496-14-9; **7**, 131588-13-1; **8**, 1083-56-3; **9**, 131567-54-9; **10**, 131567-55-0; **11**, 39253-52-6; **12**, 19096-31-2; $Co_2(CO)_8$, 10210-68-1; Ph_3P, 603-35-0; $[Co(CO)_3(PBu_3)]_2$, 14911-28-5; HC≡CH, 74-86-2; PPh_2Me, 1486-28-8; $PPhMe_2$, 672-66-2; PBu_3, 998-40-3; hexadeuteriobenzene, 1076-43-3; pentadeuteriophenyl iodide, 7379-67-1; 2-bromo-2-phenylindan-1-one, 5728-94-9.

Notes

Heterobimetallic Complexes Derived from $[(\eta^5\text{-}C_5H_5)FeCl(CH_3N(PF_2)_2)_2]$. Crystal and Molecular Structure of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2IrCl_2(P(CH_3)_2C_6H_5)]$

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Summary: The reaction of $[(\eta^5\text{-}C_5H_5)FeCl(CH_3N(PF_2)_2)_2]$ with $[Rh_2Cl_2(CO)_4]$ and $[IrCl(CO)(P(CH_3)_2C_6H_5)_2]$ forms $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2RhCl_2]$ and $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2IrCl_2(P(CH_3)_2C_6H_5)]$, respectively. The iron–iridium complex crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.901$ (2) Å, $b = 16.622$ (2) Å, $c = 32.160$ (4) Å, $Z = 8$, 3919 reflections with $I \geq 3\sigma(I)$, $R = 0.035$, and $R_w = 0.050$. The Ir–Fe distances in the two independent molecules are 2.838 (2) and 2.828 (2) Å, indicating significant metal–metal interaction.

The ligands $RN(PX_2)_2$ (R = alkyl; X = F, alkoxy, phenoxy) have been studied extensively in recent years.[1-14] Particularly with $CH_3N(PF_2)_2$, a number of binuclear[9-12] and trinuclear[4,5] complexes with unusual structures have been synthesized. As part of our continuing interest in heterobimetallic complexes stabilized by "short-bite" phosphorus ligands, we considered that $[(\eta^5\text{-}C_5H_5)FeCl(\eta^1\text{-}CH_3N(PF_2)_2)_2]$[13] should be a suitable starting point for such species.

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen with use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under nitrogen prior to use. Literature methods were used to prepare $[RhCl(COD)]_2$ (COD = cycloocta-1,5-diene),[2] $[Ir(CO)Cl(PMe_2Ph)_2]$,[15] and $[(\eta^5\text{-}C_5H_5)FeCl(\eta^1\text{-}CH_3N(PF_2)_2)_2]$.[13] ^{1}H and ^{31}P{^{1}H} NMR spectra were obtained on an IBM-Bruker AF-200 spectrometer at 200.132 and 81.015 MHz, respectively. Proton and phosphorus chemical shifts are respectively referred to tetramethylsilane (δ 0.0) and 85% H_3PO_4 (δ 0.0) with positive shifts downfield of the reference. Infrared spectra were obtained on a Mattson-Cygnus 100 Fourier transform spectrophotometer in Nujol mulls. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2IrCl_2(P(CH_3)_2C_6H_5)]$ (1). To a solution of 0.200 g (0.389 mmol) of $[Ir(CO)Cl(PMe_2Ph)_2]$ in 10 mL of toluene was added 0.191 g (0.389 mmol) of $[cpFeCl(MeN(PF_2)_2)_2]$. After it was heated at ca. 60 °C for 6 h, the solution had become a dark brown-orange. The solution was concentrated to ca. 1 mL under reduced pressure and transferred to a 1 × 20 cm column of alumina (Brockman I). The column was washed with hexane followed by elution with diethyl ether/hexane (1:1 v/v), which removed a red-orange band. Concentration of the eluate under reduced pressure afforded the product as glistening brown-orange needles. The supernatant was removed via syringe, and the crystals were washed with 2 mL of cold hexane and dried in vacuo (yield 75%). Anal. Calcd for $C_{15}H_{22}N_2P_5F_8Cl_2FeIr$: C, 21.04; H, 2.60. Found: C, 21.6; H, 2.6. ^{1}H NMR (C_6D_6): δ 7.50 (m),[16] 7.09 (m, 5 H, C_6H_5), 4.88 (t (J = 1.1 Hz), 5 H, C_5H_5), 2.22 (dd (J = 9.4, 6.2 Hz), 6 H, N–CH_3), 1.90 (d (J = 11.5 Hz), 6 H, P–CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ –19.0 (t ($^2J_{P-P}$ = 75.6 Hz)), 89.9 (tm), 191.2 (tm).

$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CH_3N(PF_2)_2)_2RhCl_2]$ (2). A suspension of 0.151 g (0.306 mmol) of $[RhCl(COD)]_2$ in 20 mL of diethyl ether was purged with carbon monoxide for several minutes and then stirred under atmosphere of carbon monoxide for 20 min. To the resulting orange solution was added 0.300 g (0.612 mmol) of $[cpFeCl(MeN(PF_2)_2)_2]$, whereupon gas evolution occurred and a dark green solid precipitated. This was filtered off, washed with diethyl ether, and redissolved in dichloromethane. Dilution of this solution with toluene and concentration under reduced pressure afforded the product as a dark green powder in essentially quantitative yield. Anal. Calcd for $C_7H_{11}N_2P_4F_8Cl_2FeRh$: C,

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