Unique Behavior of a (Ind-P)$_n$ Ligand on the Substitution Reaction of $\{\eta^5,\eta^1$-(Ind-P)$_n\}$RhCO with ^{n}Bu$_3$P

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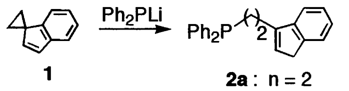
Several types of rhodium carbonyl complexes, $\{\eta^5,\eta^1$-(Ind-P)$_n\}$RhCO [(Ind-P)$_n$ = $C_9H_6(CH_2)_nPR_2$; n = 2-4; R = Ph or Cy (Cy = cyclohexyl)], have been prepared. The substitution of the carbonyl group of $\{\eta^5,\eta^1$-(Ind-P)$_{n=4}\}$RhCO with ^{n}Bu$_3$P proceeded via a novel "lid-on-off" mechanism to afford $\{\eta^5,\eta^1$-(Ind-P)$_{n=4}\}$Rh(^{n}Bu$_3$P). However, the reaction of $\{\eta^5,\eta^1$-(Ind-P)$_n\}$RhCO having an ethylene or a propylene spacer with ^{n}Bu$_3$P gave the addition products, $\{\eta^3,\eta^1$-(Ind-P)$_n\}$Rh(CO)(^{n}Bu$_3$P).

A lot of highly selective stoichiometric or catalytic reactions have been accomplished by utilizing a sterically and/or electronically controlled reaction environment around the metal center constructed of a chelate bidentate ligand having strong coordination ability.[1] The hybrid Cp-P ligand, possessing both a cyclopentadienyl and a tertiary phosphine group connected by an appropriate spacer, is one of such bidentate ligands.[2-4] Since the Cp-P ligand has two different coordination sites, it is expected to make a pliant environment around the metal and to endow the complex with a unique reactivity; the phosphine group as a weaker coordination site can coordinate on and off the central metal according to the circumstances of reactions.

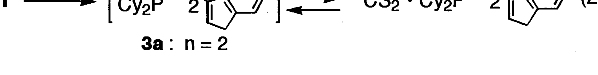
In order to investigate the reactivities of transition metal complexes having the Cp-P ligand and to apply them to organic reactions, a variety of the Cp-P ligand should be supplied.[4] The conventional synthetic procedures, however, can not produce the Cp-P ligand with various lengths of the spacer and a diversity of the substituents on the cyclopentadienyl or the phosphino groups.[2-6] Herein we report the preparation of [(Ind-P)$_n$]H ligands {[(Ind-P)$_n$]H = $C_9H_7(CH_2)_nPR_2$; n = 2-4; R = Ph or Cy (Cy = cyclohexyl)}, which are a kind of Cp-P ligand, and their rhodium complexes, $\{\eta^5,\eta^1$-(Ind-P)$_n\}$RhCO,[7] and the change of the reactivities of the complexes against ^{n}Bu$_3$P depending on the length of the spacer. Especially we have found a unique behavior of the (Ind-P)$_{n=4}$ ligand during the substitution of CO in $\{\eta^5,\eta^1$-(Ind-P)$_{n=4}\}$RhCO.

We have prepared the [(Ind-P)$_{n=2}$]H ligand **2a** by the reaction of LiPPh$_2$ with the spiro compound **1** in 45% yield (equation 1).[8] The [(Ind-P)$_{n=2}$]H ligand **3a**, having a dicyclohexylphosphino group, was similarly prepared but it was easily oxidized. Thus, **3a** was stored as the air stable CS$_2$ complex (64% isolated yield from **1**) (equation 2), from which **3a** was easily generated by just being refluxed in EtOH.[9] Another type of [(Ind-P)$_n$]H ligand **2b** or **2c**, which has a longer spacer (n = 3 or 4), was prepared by the reaction of $Ph_2P(CH_2)_nCl$[10] with C_9H_7Li in THF under reflux conditions in 21% or 28% yield based on PPh$_3$, respectively (equation 3). Each [(Ind-P)$_n$]H ligand **2a**, **2b** or **2c** was found to exist as a single isomer among the potential regioisomers from the ^{1}H and ^{31}P NMR.[11,12]



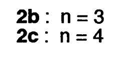
(1)

1 **2a** : n = 2



(2)

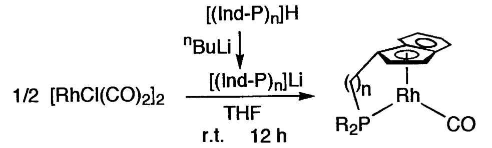
3a : n = 2



(3)

2b : n = 3
2c : n = 4

$\{\eta^5,\eta^1$-(Ind-P)$_n\}$RhCO complexes having an achiral (Ind-P)$_n$ ligand were prepared by a similar method to that previously reported by us (equation 4).[4] The mononuclear Rh(I) complex **4a** was obtained in 80% isolated yield as air stable yellow powders.[13] The presence of a terminal carbonyl group in **4a** was confirmed by the IR spectrum (1925 cm^{-1}) and the ^{13}C NMR spectrum [δ 190.5 (dd, $J_{C\text{-}Rh}$ = 89 Hz, $J_{C\text{-}P}$ = 17 Hz)]. The FAB mass spectrum of **4a** indicated the molecular ion peak at *m/e* 458. No peak due to the dimeric species was observed. Other types of $\{\eta^5,\eta^1$-(Ind-P)$_n\}$RhCO could be prepared by similar procedures (**4b**; 50%, **4c**; 71%, **5a**; 64%).[14] Different from the reaction of [RhCl(CO)$_2$]$_2$ with the lithium salt of a [Cp-P]H ligand, [$C_5H_5(CH_2)_2PPh_2$],[3] when the [(Ind-P)$_n$]H ligand was employed, only mononuclear $\{\eta^5,\eta^1$-(Ind-P)$_n\}$RhCO formed even at a low temperature of 20 °C.

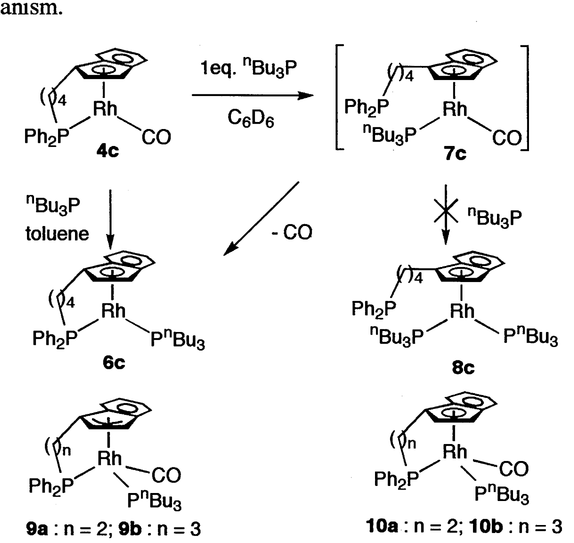


(4)

4a : R = Ph, n = 2; **4b** : R = Ph, n = 3; **4c** : R = Ph, n = 4
5a : R = Cy, n = 2

The ^{31}P NMR signal of **4a** [δ 71.1 (d, $J_{Rh\text{-}P}$ = 211 Hz)] and **5a** [δ 89.5 (d, $J_{Rh\text{-}P}$ = 197 Hz)], both having (Ind-P)$_{n=2}$ with an ethylene spacer, appeared at much lower field than those of **4b** [δ 42.0 (d, $J_{Rh\text{-}P}$ = 195 Hz)] and **4c** [δ 39.0 (d, $J_{Rh\text{-}P}$ = 203 Hz)]. This is probably due to the formation of a pseudo five-membered chelate ring, Rh-P-CH_2-CH_2-C_9H_6 in **4a** and **5a**.[15]

The rhodium complex **4c** reacted with ^{n}Bu$_3$P in toluene under reflux for 18 h to give $\{\eta^5,\eta^1$-(Ind-P)$_{n=4}\}$Rh(^{n}Bu$_3$P) **6c** quantitatively (Scheme 1).[16] When the complex **4c** was treated with one equivalent of ^{n}Bu$_3$P in C_6D_6 at 25 °C for 18 h, the ^{31}P NMR exhibited a set of two peaks of equal intensity besides the signals due to **4c** and **6c**; a doublet at δ 29.3 (d, *J* = 191 Hz) assignable to a phosphorus atom coordinated to Rh and a singlet at δ -15.4 (s). The chemical shift value of the singlet is close to that of the free [(Ind-P)$_{n=4}$]H ligand **2c**,[11] indicating that the phosphine moiety of the (Ind-P)$_{n=4}$ ligand dissociates from Rh. On heating the reaction mixture for 12 h, these signals disappeared and converted into those of **6c**. These observations suggested that $\{\eta^5$-(Ind-P)$_{n=4}\}$Rh(^{n}Bu$_3$P)(CO) **7c** was produced as an intermediate during the reaction of **4c** with $^{n}\text{Bu}_3\text{P}$ and then the dissociating phosphine of the $\text{(Ind-P)}_{n=4}$ ligand coordinated again to the Rh accompanying CO liberation to give **6c** as shown in Scheme 1. Formation of **7c** was also supported by appearance of a slightly broader CO stretching at ca. 1940 cm^{-1} for the reaction mixture obtained after 18 h at 25 °C (**4c** : **6c** : **7c** = 14% : 51% : 35% from ^{31}P NMR) different from a sharp CO stretching of the starting **4c**. The broadening of the signal may be due to the overlapping of the two CO stretching absorption of **4c** and **7c**. Even if an excess of $^{n}\text{Bu}_3\text{P}$ was employed, $\{\eta^5\text{-(Ind-P)}_{n=4}\}\text{Rh}(^{n}\text{Bu}_3\text{P})_2$ **8c** was not produced at all. It has been proposed that the carbonyl substitution of the indenyl complex, $(\eta^5\text{-C}_9\text{H}_7)\text{Rh(CO)}_2$, by a phosphine generally proceeds by an associative mechanism including an 18-electron η^3-indenyl intermediate like $\{\eta^3,\eta^1\text{-(Ind-P)}_n\}\text{Rh}(^{n}\text{Bu}_3\text{P})\text{CO}$ **9**.[17] Different from this associative mechanism, the phosphine of the $\text{(Ind-P)}_{n=4}$ ligand, which is connected to an indenyl group by a tetramethylene spacer, acted as a pendulum and the substitution reaction of the carbonyl group proceeded via a novel "lid-on-off" mechanism.



Scheme 1.

Contrary to our expectations, the reaction of **4a** or **4b**, which has a shorter spacer, with $^{n}\text{Bu}_3\text{P}$ in C_6H_6 at 20 °C did not afford the substitution products corresponding to **6c** but air- and light-sensitive oily red products. Although pure products could not be isolated due to their high solubility and instability, the spectral data indicated the formation of an η^3-indenyl addition product **9**.[18,19] The substitution of the carbonyl group of **4a** or **4b** by $^{n}\text{Bu}_3\text{P}$ did not proceed even under reflux in toluene and only **9a** or **9b** was obtained. The present spectral data can not exclude completely the possibility for a 20-electron species, $\{\eta^5,\eta^1\text{-(Ind-P)}_{n=2\text{ or }3}\}\text{Rh-}(^{n}\text{Bu}_3\text{P})\text{CO}$ **10a** or **10b** without X-ray crystallography, but it is not appropriate. The (Ind-P)_n ligands having an ethylene or a propylene spacer should coordinate more strongly to Rh(I) center as a bidentate ligand.

In summary, we have found that $\{\eta^5,\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ shows unique reactivities for CO substitution reaction different from the non-chelate cyclopentadienyl or indenyl carbonyl rhodium complexes. In addition, the reactivity changed dramatically depending on the length of the spacer. The reasons, however, are not clear at present.

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11 *e.g.* **2c**: mp: 58-59 °C. ^{1}H NMR : δ 1.49-1.65 (m, 2H), 1.76-1.90 (m, 2H), 2.06-2.15 (m, 2H), 2.49-2.59 (m, 2H), 3.27-3.31 (m, 2H), 6.12-6.16 (m, 1H), 7.15-7.47 (m, 14H). ^{31}P NMR : δ -15.3 (s). IR (nujol): 3060, 3010, 1605, 1580, 1435, 775, 755, 740, 725, 695 cm^{-1}. HRMASS (FAB): Found: *m/z* 356.1771. Calcd for $\text{C}_{25}\text{H}_{25}\text{P}$: M, 356.1694.

12 NMR spectra were recorded in CDCl_3 otherwise stated.

13 **4a**: mp: 145-148 °C (dec.). Anal. $(\text{C}_{24}\text{H}_{20}\text{OPRh})$: C, H.

14 *e.g.* **4c**: mp: 125-130 °C. ^{13}C NMR: δ 192.8 (dd, *J* = 89, 20 Hz, CO). MS (FAB): *m/z* 486 (M^{+}), 458 (M^{+}-CO). IR (nujol): 1940 cm^{-1} (νCO). Anal. $(\text{C}_{26}\text{H}_{24}\text{OPRh})$: C, H.

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16 **6c**: ^{31}P NMR (C_6D_6): δ 23.3 (dd, *J* = 209, 44 Hz, 1P), 38.6 (dd, *J* = 227, 44, 1P). MS (FAB): *m/e* 660 (M^{+}), 458 (M^{+}-$^{n}\text{Bu}_3\text{P}$).

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18 **9a**: ^{31}P NMR: δ 25.0 (dd, *J* = 209, 38 Hz, 1P), 70.9 (dd, *J* = 233, 38 Hz, 1P). ^{13}C NMR: δ 189.3 (dt, *J* = 75, 16 Hz, CO). IR (nujol): 1940 cm^{-1} (νCO).

19 A typical region of metal coordinated unsaturated carbon signals is reported to be ca. δ_C 70 ~ 100.[20] **9a** shows only three ^{13}C signals in this region [δ_C: 66.9 (dd, *J* = 3, 14 Hz), 94.9 (dd, *J* = 3, 6 Hz), 95.8 (dd, *J* = 3, 6 Hz).

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