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METAL-STABILIZED CARBANIONS

IX *. THE INFLUENCE OF METAL BASICITY ON THE $\eta^6 \rightleftarrows \eta^5$ HAPTOTROPIC EQUILIBRIUM OF (FLUORENYL)-$Cr(CO)_2L$ ANIONS ($L = CO, P(OPh)_3, PPh_3, P(n\text{-}Bu)_3$)

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Summary

The (fluorene)$Cr(CO)_2L$ complexes ($L = CO$, $P(OPh)_3$, PPh_3, $P(n\text{-}Bu)_3$) have been synthesized and metallated with KH in THF to form the corresponding η^6-anions, which in turn equilibrate at room temperature with the η^5-hapto isomers. All these species have been fully characterized by ^{13}C and ^{31}P NMR spectroscopy. The rate of metallation, the reduction potential, the IR carbonyl stretching frequencies, and the $\eta^6 \rightleftarrows \eta^5$ haptotropic equilibrium are strongly influenced by the nature of L.

Introduction

Several studies concerning the chemical properties of fluorenetricarbonylchromium complexes have been reported. These studies have involved measurements of the kinetic acidity of the methylene hydrogens [2], the rate of $\eta^6 \rightleftharpoons \eta^5$ haptotropic rearrangement in the fluorenyl anions [2,3], the ion pair behaviour between the organometallic anions and its counterion, and the effect of ring substituents on the rearrangement process [4].

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* For part VIII see ref. 1.

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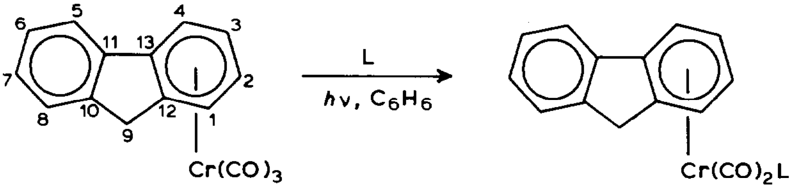
We have been interested in the effects of metal substituents on the chemistry of arene and cyclopentadienyl ligands [5] and have suggested that the methylene kinetic acidity of the fluorene species and the subsequent rearrangement processes of the chromium moiety might be sensitive to ligand substitutions on the metal. In the present paper we report the preparation of several new phosphine and phosphite fluorenedicarbonylchromium derivatives and describe the effects of these ligands on the kinetic acidities of the fluorene methylene protons and on the position of the $\eta^6 \rightleftarrows \eta^5$ haptotropic equilibrium in the anions. The neutral species and both η^6- and η^5-anionic species have been fully characterized by IR and ^{13}C and ^{31}P NMR spectroscopy.

Results and discussion

Synthesis and characteristics of the neutral complexes

The introduction of phosphine or phosphite in place of carbonyl ligands was readily accomplished by photolysis of fluorenetricarbonylchromium complex (I) with the appropriate phosphine or phosphite in benzene solution.



(I)

(II, L = P(OPh)$_3$;
III, L = PPh$_3$;
IV, L = P(n-Bu)$_3$)

Compounds II–IV were obtained in good yield, and were isolated as crystalline solids which gave good analysis. The mass spectra showed the molecular ions for all the complexes.

TABLE 1

METALLATION RATE CONSTANTS, k, VOLTAMMETRIC REDUCTION POTENTIALS, E, AND IR FREQUENCIES, $\nu(C{\equiv}O)$, FOR (FLUORENE)Cr(CO)$_2$L DERIVATIVES (L = C≡O, P(OPh)$_3$, PPh$_3$, P(n-Bu)$_3$)

L	10^2 k (s^{-1}) [a]	E (V) [b]	$\nu(C{\equiv}O)$ (cm^{-1}) [c]		
			Neutral	η^6-anion [d]	η^5-anion [d]
CO	7.8 ± 0.2	−1.92	1968,1895	1920,1829,1788	1899,1799,1755
P(OPh)$_3$	8.1 ± 0.6	−2.04	1913,1862	1857,1789	1816,1736
PPh$_3$	2.0 ± 0.1	−2.12	1891,1839	1826 [e],1756	1748 [f],1706 [f]
P(n-Bu)$_3$	1.1 ± 0.1	−2.28	1880,1829	1810,1720 [e]	–
Free fluorene	6.4 ± 0.9	−2.56	–	–	

[a] THF solution, T 294.0 ± 0.1 K. [b] Solvent, dimethylformamide; supporting electrolyte, tetraethylammonium perchlorate; potential sweep rate, 0.25 V s^{-1}; the potentials are shown against an Ag,AgCl in tetramethylammonium chloride-saturated acetonitrile/dimethylformamide 3/1 v/v solution, $E_{Ag,AgCl,Cl} - E_{SCE} = 0.31 \pm 0.01$ V. [c] THF solutions, $\Delta\nu = \pm 1$ cm^{-1} unless otherwise stated. [d] Counter ion K^+. [e] $\Delta\nu = \pm 2$ cm^{-1}. [f] $\Delta\nu = \pm 4$ cm^{-1}.

TABLE 2

^{13}C [a] AND ^{31}P [b] CHEMICAL SHIFTS FOR THE (FLUORENE)Cr(CO)$_2$L COMPLEXES [c] (L = CO, P(OPh)$_3$, PPh$_3$, and P(n-Bu)$_3$)

	I [d]	II [e]	III [e]	IV [e]
C(1)	91.6	88.26	86.11	84.13
C(2)	93.1	89.93	91.59	88.81
C(3)	92.0	88.67	89.36	86.09
C(4)	87.9	84.98	85.91	82.88
C(5)	120.9	120.84	120.68	120.02
C(6)	129.1	128.34	127.81	127.26
C(7)	127.9	127.52	127.33	127.26
C(8)	127.5	125.37	125.44	125.33
C(9)	37.5	37.10	37.27	37.49
C(10)	143.2	143.23	143.45	143.19
C(11)	139.7	140.56	141.54	142.25
C(12)	114.3	110.63	107.32	107.43
C(13)	112.0	108.09	105.35	104.51
C≡O	234.3	236.38 [f] 236.68 [f]	240.39 [f] 240.92 [f]	240.46 [f] 241.26 [f]
^{31}P	–	199.3	92.6	63.3

[a] ^{13}C shifts are in ppm from internal Me$_4$Si. For carbon numbering see text. [b] ^{31}P shifts are in ppm from external 85% aqueous H$_3$PO$_4$. [c] In THF, T 301 K. [d] Data from ref. 2. [e] Phosphorus ligand carbon chemical shifts ($J(^{13}C-^{31}P)$ coupling constants in parentheses, Hz); II: *o,o′* 122.60 (4.6), *m,m′* 130.07 (0.0), *p* 124.70 (1), *j* 153.45 (6.3); free P(OPh)$_3$: *o,o′* 121.26 (7.0), *m,m′* 130.23 (0,0), *p* 124.75 (1.1), *j* 152.40 (3.0); III: *o,o′* 133.81 (10.2), *m,m′* 128.44 (9.2), *p* 129.43 (0.0), *j* 140.84 (33.3); free PPh$_3$: *o,o′* 134.26 (19.3), *m,m′* 129.05 (7.3), *p* 129.84 (0.0), *j* 138.20 (11.7); IV: α 30.53 (19.4), β ca. 26 (hidden by THF resonance), γ 25.35 (12.0), δ 14.15 (0.0); free PBu$_3$: α 29.30 (13.8), β 28.60 (14.8), γ 25.40 (11.1), δ 14.70 (0.0). [f] $^2J(^{13}C-^{31}P)$, Hz: II 33.0; III 20.3; IV 21.3.

The carbonyl stretching frequencies, Table 1, decrease in the order CO > P(OPh)$_3$ > PPh$_3$ > P(n-Bu)$_3$ as expected from other measures of the electron-donating abilities of these phosphorous ligands [6]. The peak potentials in cyclic voltammetry for the reduction of these compounds in dimethylformamide solution show that the difficulty of electron addition to the neutral systems increases in the same order (see Table 1). Both results are consistent with an increase in electron density at the metal on going from compound I to compound IV.

As can be seen from Table 2, the replacement of one carbonyl by a phosphorus ligand causes a sensitive upfield shift of the ^{13}C NMR signal in the spectra of the fluorene carbon atoms of the complexed ring, whereas the carbonyl resonances are shifted downfield. These effects increase as the basicity of the phosphorus ligand increases. No appreciable substituent effects are observed in the uncomplexed ring of fluorene. It is noteworthy that, because of the coupling with phosphorus and their diastereotopic nature, the carbonyl ligands exhibit a spectrum split into two doublets (see Table 2). No coupling between phosphorus and fluorene carbon nuclei was detected.

Production of the anions and haptotropic rearrangement

Reaction of the fluorenetricarbonylchromium complex with KH in oxygen-free, dry THF under argon atmosphere was found to lead cleanly to the corresponding

TABLE 3

^{13}C [a] AND ^{31}P [b] CHEMICAL SHIFTS FOR η^6- AND η^5-FLUORENYL-Cr(CO)$_2$L ANIONS [c] (L = CO, P(OPh)$_3$, PPh$_3$, and P(n-Bu)$_3$)

	Ia [d]	Ib [d]	IIa [e]	IIb [e]	IIIa [e]	IIIb [e]	IVa [e]
C(1)	85.2	122.6	84.97	122.46	85.98	122.05	81.40
C(2)	94.5	125.4	92.91	125.75	93.44	126.5	92.81
C(3)	77.1	118.1	78.14	118.36	79.00	117.52	74.71
C(4)	93.5	125.2	92.61	125.16	92.27	126.4	89.20
C(5)	119.5	125.2	119.98	125.16	119.96	126.4	118.76
C(6)	113.0	118.1	112.37	118.36	111.62	117.52	11.90
C(7)	122.7	125.4	123 [f]	125.75	122.05	126.5	121.39
C(8)	117.6	122.6	117.04	122.46	117.05	122.05	116.64
C(9)	83.1	63.0	81.72	63.80	81.57	63.83	80.14
C(10)	143.3	110.9	142.77	109.30	142.80	111.00	142.55
C(11)	126.6	99.1	126.00	98.33	126.40	97.75	127.63
C(12)	122.6	110.9	122.27	109.30	120.57	111.00	122.26
C(13)	92.7	99.1	91.24	98.33	91.05	97.75	89.93
C≡O	240.3	246.0	242.43 [g] 243.34 [g]	247.92 [g]	246.93 [g] 247.62 [g]	252.75 [b]	245.56 [g] 245.70 [g]
^{31}P	–	–	202.0	201.3	99.7	107.8	64.7

[a] ^{13}C shifts we in ppm from internal Me$_4$Si. For carbon numbering see text. [b] ^{31}P shifts are in ppm from external 85% aqueous H$_3$PO$_4$. [c] In THF, counter ion K$^+$, T 301 K. [d] Data from ref. 2. [e] Phosphorus ligand carbon chemical shifts ($J(^{13}C-^{31}P)$ coupling constants in parentheses, Hz); IIa: *o,o′* 122.95 (4.6), *m,m′* 129.48 (0.0), *p* 123.71 (ca. 1), *j* 154.37 (5.5); IIb: *o,o′* 122.67 (4.6), *m,m′* 129.17 (0.0), *p* 122.79 (ca. 0), *j* 154.77 (6.5); IIIa: *o,o′* 134.13 (11.1), *m,m′* 127.66 (8.3), *p* 128.10 (0.0), *j* 142.71 (28.7); IIIb: *o,o′* ca. 143, and *p* ca. 128 (hidden by resonances of IIIa), *m,m′* 127.13 (8.3), *j* 142.50 (28.7); IVa: α 27.38 (16.6), β 26.76 (11.1), γ 25.44 (12.0), δ 14.4 (0.0). [f] Hidden by phosphite resonances. [g] $^2J(^{13}C-^{31}P)$, Hz: IIa 36.0; IIb 36.0; IIIa 20.3; IIIb 20.3; IVa 21.3.

anion. The rates of metallation were determined by monitoring the evolution of hydrogen gas; details of this procedure have been described previously [2]. In the study, the pseudo-first order rate constants for the formation of the η^6-anions (Ia–IVa) at 294 K (Table 1) were found to decrease in the order: CO ≃ P(OPh)$_3$ > PPh$_3$ > P(n-Bu)$_3$. Comparison of these rates with that for the uncomplexed fluorene at the same temperature, namely $k = (6.5 \pm 0.9) \times 10^{-2}$ s^{-1}, illustrates the extent to which the electron-withdrawing character of the chromium moiety can be modified by ligand substitution.

Quenching of the anion solutions with oxygen-free water or methanol regenerates the starting complex in good yield (≥ 90%). Traces of oxygen were found to react with the anions to form several minor products, including the chromium-substituted fluorenone complexes. Reaction of the fluorenyl anion with oxygen has been shown to produce fluorenone [7].

^{13}C and ^{31}P NMR spectra at −20 °C of the anions produced from I to IV show only the anionic η^6-species, Ia–IVa. When the solutions of these anions were warmed from −20 to +30 °C, carbon and phosphorus signals associated with η^5-species (Ib, IIb, and IIIb, see Tables 3) were observed to appear progressively in the spectra. No resonances which could be associated with η^5-hapto isomer were found in the spectrum of the anion IVa. The ^{13}C and ^{31}P chemical shift data for the anions are listed in Table 3.

The ^{1}H NMR spectra were also recorded for the neutral complexes and the corresponding η^6-anions (see Experimental). The ^{1}H NMR spectra of η^5-hapto isomers could not be resolved. A detailed analysis of the proton spectra together with differential Nuclear Overhauser Effect studies on these systems to determine their solution conformations is in progress, and will be described separately.

The remarkable downfield shift of the carbonyl resonances observed when the η^6-anionic species are formed indicates a substantial transfer of negative charge from the fluorenyl anion to the inorganic moiety. This effect is further enhanced in the observed η^5-hapto isomers, Ib, IIb, and IIIb (see Table 3). Because of the mirror symmetry of the molecule in the η^5-isomers, the carbonyl ligands are no longer diastereotopic, and their spectrum appears as a single doublet.

A downfield shift is also found for the ^{31}P NMR signals on going from the neutral to the η^6-anions, while the ^{31}P chemical shift changes on going from η^6 to η^5 anions do not show a simple pattern. It has been already found that ^{31}P chemical shifts in the series $(C_6H_5R)Cr(CO)_2PPh_3$ are sensitive to the identity of R, and the signals tend to move downfield as the electron-donating ability of R is increased [8].

The transmission of the negative charge density from the fluorenyl system to the chromium moiety is also monitored by the lowering of the carbonyl stretching frequencies on going from the neutral to the η^6- and then to the η^5-anionic species (Table 1).

From the ^{13}C and ^{31}P spectra it was possible to determine the position of the $\eta^6 \rightleftarrows \eta^5$ equilibrium. The equilibrium ratios observed, η^5/η^6, at 30 °C were:

$CO > P(OPh)_3 > PPh_3 > P(n\text{-}Bu)_3$
7 0.25 0.10 0

The low concentration of the η^5 species in the dicarbonylchromium anions precluded measurements of the rate of the rearrangement. However, qualitative observations suggest that the migration rates for the phosphine and phoshite derivatives are slower than that for the tricarbonylchromium complex.

As shown above, the substitution of phosphine or phosphite ligands for carbonyl ligands results in an increase in the electron density at the metal. Analogous results in respect of the changes of spectroscopic [6] and polarographic [9] properties induced by the replacement of carbonyl ligands were previously obtained for different substrates. Moreover, we previously showed that the Taft substituent constants of (arene)$Cr(CO)_2L$ complexes are sensitive to the identity of L [5]. The present work is the first illustration of a change in some chemical properties, viz. the kinetic acidity and the haptotropic equilibrium constant, upon variation of the ligand in the inorganic moiety. The observed decrease in kinetic acidity for the series of compounds I–IV follows the order of increased electron density at the metal, and can be understood in terms of a reduction of the electron withdrawal usually associated with a tricarbonylchromium moiety. This observation suggests that by judicious selection of metal ligands it might be possible to fine tune the kinetic acidity, and hence the reactivity, of benzyl hydrogens in other compounds.

The modifications to the $\eta^6 \rightleftarrows \eta^5$ haptotropic equilibrium ratios also follow the order of increased electron density at the metal. Steric effects do not appear to be involved in these modifications, since the order of cone angle of the phosphine and phosphite ligands is [10]:

$P(OPh)_3 > P(n\text{-}Bu)_3 > PPh_3$
128° 132° 145°

Our inability to measure the rates of rearrangement prevents us from assessing the effect of ligand substitution on the energy barrier to the metal migration. Despite this, it is clear from the equilibrium data that the η^6 is stabilized relative to the η^5 species as the electron-withdrawing ability of the chromium moiety decreases. If it is assumed that the ΔS differences for the haptotropic equilibrium are small on passing from the $Cr(CO)_3$ to the $Cr(CO)_2L$ complexes, the observed equilibrium changes reflect a net stabilization of 8–10 kJ mol^{-1} for the η^6-species of the substituted compound. Detailed theoretical analysis of the potential energy surfaces of the two hapto isomers will be necessary to establish the precise nature of this stabilization.

In a recent study of the rates and thermodynamic activation parameters for the haptotropic rearrangement of the η^6-(fluorenyl)-$Mn(CO)_2L$ to the η^5-(fluorenyl)$Mn(CO)_2L$ neutral complexes reported by Basolo et al. [11], no significant change in activation parameters was found on going from L = CO to L = $P(n\text{-}Bu)_3$, showing that the rate of metal migration is not affected by the metal basicity. In both cases the haptotropic rearrangement is complete and irreversible. It is not possible at present to compare these activation parameters derived from rate studies with the equilibrium data reported here.

Additional work is now in progress to determine the effect of ligand substitution on other properties of arenechromium complexes, and to extend the present investigation to other well-characterized haptotropic rearrangements.

Experimental

Melting points are uncorrected. Microanalyses were performed by Mr. L. Turiaco, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova. IR, UV, and mass spectra were recorded with a Perkin–Elmer 580B, a Varian DMS-80, and a VG MM 16 spectrometers, respectively. The voltammetric measurements were made with an EG&G Princeton Applied Research electrochemical instrument comprised of a model 173 potentiostat equipped with a model 175 function generator, a 4203 signal averager, and a RE 0074 XY recorder. The ^1H NMR spectra were recorded on a Bruker WP-80 SY and the ^{13}C and ^{31}P NMR spectra on a Bruker WP-200 SY spectrometer. The ^{13}C line assignments were based on standard ^{13}C correlations and use of off-resonance and partially relaxed spectra and selective proton decoupling experiments.

Commercial grade fluorene was crystallized from ethanol and sublimed in vacuo. Fluorenetricarbonylchromium (I) was prepared by standard methods from the ligand and $Cr(CO)_6$ in boiling diglyme, and recrystallized from diethyl ether/hexane under argon [2].

Synthesis and characterization of fluorene-$Cr(CO)_2L$ complexes

The phosphine and phosphite derivatives, II–IV, were obtained by UV irradiation of benzene solutions of I in the presence of the appropriate phosphorus ligand, as described in ref. 12. The IR $\nu(C\equiv O)$ frequencies for the products are listed in Table 1, and ^{13}C and ^{31}P NMR data are listed in Table 2. Other physical and spectroscopic data are mentioned below.

Fluorene(dicarbonyltriphenylphosphite)chromium (II, nc)

Golden-yellow crystals. M.p. 123–125 °C. (Found: C, 67.70; H, 4.34. $C_{33}H_{25}CrO_5P$ calc: C, 67.81; H, 4.31%). UV (in THF), λ_{max} (log ϵ): 238 (4.35), 244 (4.35), 253 (4.36), 260 (4.19), 337 (3.98), and 393sh nm (3.37). Mass spectrum: M^+ 584 (calc: 584). ^1H NMR (acetone-d_6, T 298 K, Me_4Si), δ (ppm): 7.4–7.2 (19H, m, $P(OPh)_3$ and fluorene uncomplexed ring protons), 5.61 (1H, d, H(4), $J_{3,4}$ 6.3 Hz), 5.04 (1H, d, H(1), $J_{1,2}$ 6.3 Hz), 4.64 (1H, tdd, H(3), $J_{2,3} \sim J_{3,4} = 6.3$, $J_{P,3}$ 4.5, and $J_{1,3} \sim 1$ Hz), 4.44 (1H, tdd, H(2), $J_{1,2} \sim J_{2,3} \sim J_{P,2}$ 3.5, and $J_{2,4} \sim 1$ Hz), 3.67 (2H, AB quartet, H(9), H(9′), J_{AB} 21.7 Hz).

Fluorene(dicarbonyltriphenylphosphine)chromium (III, nc)

Red-orange crystals. M.p. 149 °C (dec.). (Found: C, 73.96; H, 4.67. $C_{33}H_{25}CrO_2P$ calc: C, 73.87; H, 4.70%). UV (in THF), λ_{max} (log ϵ): 222sh (4.66), 227sh (4.58), 244 (4.49), 253 (4.52), 264sh (4.17), 290 (3.80), 300 (3.80), and 352 nm (3.98). Mass spectrum: M^+ 536 (calc: 536). ^1H NMR (acetone-d_6, T 298 K, Me_4Si), δ (ppm): 7.6–7.2 (19H, m, PPh_3 and fluorene uncomplexed ring protons), 5.57 (1H, d, H(4), $J_{3,4}$ 6.2 Hz), 5.30 (^1H, d, H(1), $J_{1,2}$ 6.2 Hz), 4.87 (1H, tdd, H(2), $J_{1,2} \sim J_{2,3} = 6.2$, $J_{P,2}$ 3.0, $J_{2,4} \sim 1$ Hz), 4.45 (1H, tdd, H(3), $J_{2,3} = J_{3,4} = 6.2$, $J_{P,3}$ 3.4, $J_{1,3} \sim 1$ Hz), 3.92 (2H, AB quartet, H(9), H(9′), J_{AB} 21.7 Hz).

Fluorene (dicarbonyltri-n-butylphosphine)chromium (IV, nc)

Red crystals. M.p. 73 °C (dec.). (Found: C, 67.57; H, 8.53. $C_{27}H_{37}CrO_2P$ calc: C, 68.05; H, 7.83%). UV (in THF), λ_{max} (log ϵ): 244 (4.82), 253 (4.80), 264sh (4.62), 272 sh (4.51), 288 (3.84), 293 (3.82), 300 (3.83), 309sh (3.76), and 350 nm (3.90). Mass spectrum: M^+ 476 (calc: 476). ^1H NMR (acetone-d_6, T 298 K, Me_4Si), δ (ppm): 7.7–7.1 (4H, m, fluorene uncomplexed ring protons); 5.81 (1H, dd, H(4), $J_{3,4}$ 6.2, $J_{P,4}$ 3.4 Hz); 5.34 (1H, d, H(1), $J_{1,2}$ 6.1 hz); 5.09 (1H, tdd, H(2), $J_{2,3} \sim J_{1,2} = 6.2$, $J_{P,2}$ 2.6, $J_{2,4} \sim 1$ Hz); 4.92 (1H, tdd, H(3), $J_{2,3} \sim J_{3,4} = 6.2$, $J_{P,2}$ 2.6, $J_{2,4} \sim 1$ Hz); 4.92 (1H, tdd, H(3), $J_{2,3} \sim J_{3,4} = 6.2$, $J_{P,3}$ 3.0, $J_{1,3} \sim 1$ Hz); 3.91 (2H, H(9), H(9′) AB quartet, J_{AB} 21.4 Hz).

Preparation, NMR and IR spectra, and quenching of the anions with electrophiles

Samples of the anions IIa–IVa for NMR measurements were prepared under argon by treating THF-d_8 solutions of the neutral complexes with an excess of KH, as previously described [2], (ca. 0.05 *M* for ^1H and ^{31}P measurements, and ca. 0.3 *M* for ^{13}C). A first order ^1H NMR analysis gives the following parameters for the anions IIa–IVa.

IIa (in THF-d_8, T 298 K, Me_4Si), δ (ppm): 7.8 (1H,d, H(5), $J_{5,6}$ 7.6 Hz) 7.6–6.9 (17H, m, H(7), H(8), and $P(OPh)_3$ protons); 6.6 (1H, t, H(6), $J_{5,6} \sim J_{6,7} \sim 7.6$ Hz); 6.33 (1H, d, H(4), $J_{3,4}$, 6.2 Hz); 5.43 (1H, s, H(9)); 5.02 (1H, d, H(1), $J_{1,2}$ 6.9 Hz); 4.7 (1H, rough quartet, H(2), $J_{1,2}$ 6.9 and $J_{2,3} \sim J_{P,2} \sim 6$ Hz); 3.57 (1H, broad triplet, H(3), $J_{2,3} \sim J_{3,4} \sim 6.2$, $J_{P,3} \sim 3$ Hz).

IIIa (in THF-d_8, T 298 K, Me_4Si), δ (ppm): 7.70 (1H, d, H(5), $J_{5,6}$ 7.6 Hz); 7.4–6.7 (17H, m, H(7), H(8), and PPh_3 protons); 6.55 (1H, t, H(6), $J_{6,7} \sim J_{5,6} = 7.6$ Hz); 6.28 (1H, d, H(4), $J_{3,4}$ 6 Hz); 5.36 (1H, s, H(9)); 5.27 (1H,d, H(1), $J_{1,2}$ 6.5 Hz); 4.72 (1H, broad t, H(1); $J_{1,2} \sim J_{2,3} \sim 6.5$ and $J_{P,2} \sim 3$ Hz); 4.17 (1H, broad t, H(3), $J_{3,4} \sim J_{2,3} \sim 6$ and $J_{P,3} \sim 1$ Hz).

IVa (in THF-d_8, T 298 K, Me_4Si), δ (ppm): 7.67 (1H, d, H(5), $J_{5,6}$ 7.7 Hz); 7.16 (1H, d, H(8), $J_{7,8}$ 8.0 Hz); 6.84 (1H, ddd, H(7), $J_{7,8}$ 8.0, $J_{6,7}$ 6.7, and $J_{2,4}$ 1.2 Hz);

6.51 (1H, ddd, H(6), $J_{5,6}$ 7.7, $J_{6,7}$ 6.7 and $J_{6,8} \sim 1$ Hz); 6.43 (1H, d, H(4), $J_{3,4}$ 5.7 Hz); 5.34 (1H, d, H(9), $J_{P,9} \sim 1$Hz); 5.39 (1H, dd, H(1), $J_{1,2}$ 6.8, $J_{P,1} \sim 2$ Hz); 5.10 (1H, ddd, H(2), $J_{1,2}$ 6.8, $J_{2,3}$ 5.7, and $J_{2,4} \sim 1$ Hz); 4.21 (1H, t, H(3), $J_{2,3} = J_{3,4}$ 5.7 Hz).

The ^{13}C and ^{31}P NMR chemical shifts are shown in Table 3.

For H_2 evolution measurements, ca. 10^{-2} *M* solutions of the neutral complexes in THF were treated with an excess of KH under argon at 294.0 ± 0.1 K. The pseudo-first order constants, *k*, are shown in Table 1. Aliquots of the anion solutions obtained were transferred under argon to a dry, argon-flushed IR cell (CaF_2 windows, 0.2 mm optical path), and the spectra recorded between 2000 and 1700 cm^{-1}.

Quenching with oxygen-free water- or methanol-containing THF of the anion solutions, whether freshly prepared or allowed to reach equilibrium, regenerated the initial neutral complexes II–IV.

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