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Stereochemistry in group 5 organometallic complexes: a metallophosphine with an asymmetric tantalum centre as precursor of chiral bimetallic derivatives

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Summary — A trisubstituted cyclopentadiene derivative **2** is synthesized and used as a cyclopentadienyl ligand to obtain the tantalum (IV) derivative $Cp'CpTaCl_2$ **5**. Starting from this dichloride, a multistep transformation (reduction, carbonylation and reaction with PMe_2Cl) leads to the chiral metallophosphine **9** which contains an asymmetric tantalum centre. This metalloligand reacts with a carbonyl chromium fragment giving a chiral bimetallic derivative.

trisubstituted cyclopentadiene / tantalum / chiral metallophosphine / bimetallic complex

Résumé — Stéréochimie dans les complexes organométalliques du groupe 5: une métallophosphine avec un tantale asymétrique comme précurseur de dérivés bimétalliques chiraux. *Un dérivé trisubstitué* **2** *du cyclopentadiène est synthétisé et utilisé comme ligand cyclopentadiényle pour obtenir le dérivé du tantale (IV)* $Cp'CpTaCl_2$ **5**. *A partir de ce dichlorure, une transformation en plusieurs étapes (réduction, carbonylation et réaction avec* PMe_2Cl*) conduit à la métallophosphine* **9** *dans laquelle le tantale est centre d'asymétrie. Ce métalloligand réagit avec un fragment chrome carbonyle pour donner un dérivé bimétallique chiral.*

cyclopentadiène trisubstitué / tantale / métallophosphine chirale / complexe bimétallique

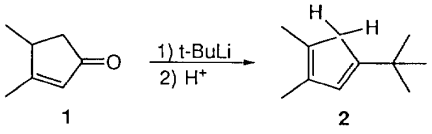
Introduction

The stereochemistry of organometallic complexes has developed greatly during the two last decades. Brunner [1] and Sokolov [2] described the most significant data in this field and gave numerous examples of tetrahedral, pyramidal and octahedral mononuclear structures containing a chiral metallic centre. Bi- and polymetallic structures can also exhibit chirality, but well-characterized examples are as yet scarce [3]. Interest in this area is obvious for catalytic or stoichiometric enantioselective transformations. For some years, we have been developing a new synthetic approach to bimetallic systems involving group 5 and 6 terminal phosphido complexes [4]. These metallophosphines contain the Cp_2M moiety while stereochemical studies require the use of Cp'CpM fragments. The efficient synthesis of chiral complexes requires the introduction of significant stereodifferentiation between the Cp' and Cp cyclopentadienyl ligands; from this point of view, monosubstituted ($Cp' = C_5H_4R$) or peralkylated (C_5R_5) ligands are suitable, however some recent observations [5] have suggested using different ring substituted ligands.

We therefore undertook the synthesis of a new trisubstituted cyclopentadiene and would like to report here its use in accessing mono- and bimetallic chiral complexes.

Results and discussion

Addition of *t*-BuLi to 3,4-dimethylcyclopent-2-enone **1** followed by aqueous HCl treatment produces the cyclopentadiene derivative **2** (scheme 1) which is shown to be reasonably pure by ^1H and ^{13}C NMR spectroscopy. Attempts to obtain further purification by distillation lead to significant destruction of the material and only poor yields of the pure product can be recovered. **2** exists as a single isomer, 1,2-dimethyl-4-(*t*-butyl) cyclopentadiene: the presence of a singlet at 2.66 ppm (in C_6D_6) compared with that found at 2.60 ppm for the 1,2,3,4-tetramethylcyclopentadiene [6] clearly signals that the C-5 carbon is unsubstituted. In contrast, tri-*tert*-butylcyclopentadiene exists as the 1,3,5-isomer and such an arrangement results from the steric bulk of the *tert*-butyl substituants [7]. Consistent with the mentioned structure for **2**, a triplet ($^1J_{CD} = 18.4$ Hz) was



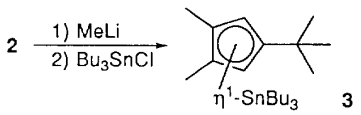
1 2

Scheme 1

* Correspondence and reprints

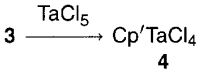
recorded for the ring C-5 carbon when $C_5H_2Me_2t$-BuLi was quenched with D_2O.

It is now well established that the easiest method to synthesize a monocyclopentadienyl tantalum derivative is to use a tributyltin compound [8]. **3** is obtained after deprotonation of **2** with MeLi by addition of Bu_3SnCl (scheme 2). Unlike **2**, ^1H and ^{13}C NMR spectra of **3** reveal the presence of a symmetrical product; the ^1H NMR spectrum is not affected by cooling the sample down to −60 °C in toluene. Although the tin moiety is ring
σ-bonded, the symmetry of the spectrum probably results from a rapid metallotropic rearrangement rather than a single symmetrical position of the tin atom; such an intramolecular migration process appears be the general behavior with group 14 elements [9]. **3** is thermally stable and can be conserved for a long time under argon.

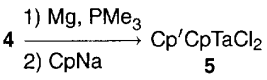


Scheme 2

Addition of **3** to a suspension of $TaCl_5$ in pentane gives the expected tantalum (V) derivative **4** in a good yield (scheme 3). Although the preparation of some niobium (IV) complexes containing two different cyclopentadienyl ligands have been reported [10], to date no general procedure concerning tantalum derivatives is known; Bercaw's method has only been used for complexes such as $Cp'CpTaCl_2$ where Cp′ is a pentaalkylated ligand [11, 5b]. In some other cases (Cp′ = C_5H_4R), an exchange of ligands occurs during the introduction of the second ring, resulting in the formation of an inseparable mixture of Cp'_2TaCl_2, Cp_2TaCl_2 and the expected $Cp'CpTaCl_2$ [12]. After reduction of **4** by Mg in the presence of PMe_3, we found that addition of CpNa gave only the expected mixed-ring product **5** (scheme 4). **5** displays the eight-line ESR spectrum characteristic of biscyclopentadienyl tantalum (IV) derivatives [13].

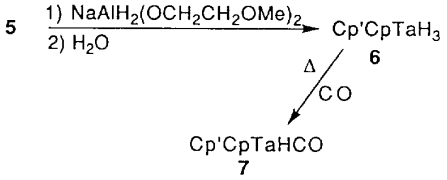


Scheme 3

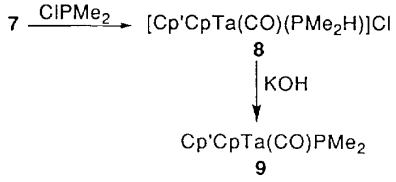


Scheme 4

The complex **5** is treated with $NaAlH_2(OCH_2CH_2OMe)_2$ in toluene and after hydrolysis and extraction, crystallization in toluene affords white crystals of **6** (scheme 5). Heating of **6** in decane under an atmosphere of carbon monoxide gives the purple carbonyl species **7** (scheme 5) which is purified by sublimation. According to a procedure previously described [14], monohydride **7** reacts quickly with chlorodimethylphosphine to afford the water-soluble phosphonium salt **8**, which leads to the neutral metallophosphine **9** upon treatment with aqueous KOH solution (scheme 6). Table I summarizes the main spectroscopic data of hydrides **6**, **7** and phosphorus compounds **8** and **9**.



Scheme 5



Scheme 6

The expected hydride resonances in **6** and **7** as well as the IR-ν_{CO} absorption of **7** fall between those observed for the Cp_2Ta [15] and Cp^*_2Ta [11] ($Cp^* = C_5Me_5$) analogues. However, these values are closer to those of the corresponding peralkylated compounds and are consequently indicative of the efficient electrodonating power of the Cp′ ligand. Significant differences in the ^1H and ^{13}C chemical shifts are found for the complexes **7**, **8** and **9**; namely, a progressive deshielding of the Cp resonance signals is observed when going from **7** to **9** to **8**. The same sequence shows increasing IR ν_{CO} frequencies: all these data agree with a decreasing electron density at the tantalum atom.

Due to the asymmetric metal centre in the chiral metallophosphine **9**, a large anisochrony is found for the two protons as well as for the two methyl groups in the Cp′ ligand. It is noteworthy that only one proton signal is coupled with the phosphorus nucleus, probably for conformational reasons. The PMe_2 resonance is temperature dependant: it appears as a very broad singlet at 295 K and as a doublet ($^2J_{PH}$ = 4 Hz) at 330 K, whereas two well resolved doublets ($\Delta\nu$ = 56 Hz, $^2J_{PH}$ = 4 Hz) are observed when the temperature is decreased to 260 K. Such behavior is indicative of a lack of stereostability either at the metal centre or at the phosphorus atom; however a variable temperature NMR study performed on the phosphonium derivative **8** showed no significative change in the spectra, and therefore it can be assumed that the 'racemization process' involves the phosphorus atom by a rapid inversion of the lone pair. The ΔG value has been estimated to be 58 KJ mol^{-1} (Eyring equation); this value is close to that found for similar niobio derivatives [16].

In order to obtain chiral bimetallic structures, we exposed the metallophosphine **9** to a chromium pentacarbonyl fragment (scheme 7). The bimetallic complex **10** was obtained in a good yield and has been fully characterized spectroscopically (table II).

Table I. Spectroscopic data of $Cp'CpTaH_3$ **6**, Cp'CpTaH(CO) **7**, $[Cp'CpTa(CO)PMe_2H]Cl$ **8**, $Cp'CpTa(CO)PMe_2$ **9**.

Compounds		**6**[a]	**7**[a]	**8**[b]	**9**[a]
^{1}H NMR					
Cp		4.79 (s, 5)	4.50 (s, 5)	5.43 (d, J_{C_pP} =2 Hz, 5)	4.46 (s, 5)
Cp′	C*H*	4.51 (s, 2)	4.14–4.09 (m, 2)	5.43 (*, 1) 4.98 (s, br, 1)	4.39 (dd, J_{PH} = 7 Hz, $^4J_{HH}$ = 2.5 Hz, 1) 3.82 (d, $^4J_{HH}$ = 2.5 Hz, 1)
	CH_3	1.88 (s, 6)	1.84 (s, 3) 1.80 (s, 3)	2.13 (s, 3) 2.01 (s, 3)	2.03 (s, 3) 1.94 (s, 3)
	$(CH_3)_3$	1.27 (s, 9)	1.16 (s, 9)	1.13 (s, 9)	0.97 (s, 9)
Others		−0.95 (t, $^2J_{HH}$ = 10.2 Hz, 1, Ta*H*) −2.50 (d, $^2J_{HH}$ = 10.2 Hz, 2, Ta*H*);	−6.20 (s, 1, Ta*H*)	5.11 (dh, $^1J_{PH}$ = 356 Hz, $^3J_{HH}$ = 6.5 Hz, 1, P*H*); 1.62 (dd, $^2J_{PH}$ = 10.2 Hz, $^3J_{HH}$ = 7.0 Hz, 3, P*Me*); 1.53 (dd, $^2J_{PH}$ = 10.0 Hz, $^3J_{HH}$ = 7 Hz, 3, P*Me*)	1.50 (s, br, 6, P*Me*)
^{13}C NMR					
Cp		87.2	84.4	92.9	88.9
Cp′	ring	124.1, 102.3, 83.8	117.9, 103.7, 96.0, 83.6, 81.7	127.8, 104.4, 101.6, 97.3, 89.2	120.6, 104.3, 97.7, 96.5, 84.4
	$C(CH_3)_3$	31.0	31.6	34.5	32.4
	$C(CH_3)_3$	32.3	32.4	33.7	32.1
	CH_3	14.3	14.5, 13.8	14.5, 13.5	13.3, 12.4
CO			267.2	246.0 (d, $^2J_{PC}$ = 8 Hz)	261.1
PMe_2				15.8 (d, $^1J_{PC}$ = 21.6 Hz) 15.1 (d, $^1J_{PC}$ = 15.2 Hz)	18.7 (d, $^1J_{PC}$ = 29.2 Hz, br)
^{31}P NMR					
PMe_2				−45.7 (d, $^1J_{PH}$ = 356 Hz)	−91.5
IR (THF)					
ν_{CO} (cm^{-1})			1 881 s	1 916 s	1 891 s

[a] In C_6D_6 (295 K), ^{1}H and ^{13}C NMR (δ (ppm)/TMS), ^{31}P NMR (δ (ppm)/H_3PO_4). [b] In D_2O (295 K), ^{1}H and ^{13}C NMR (δ (ppm)/TMSP), ^{31}P NMR (δ (ppm)/H_3PO_4). * Signal masked by the signal of Cp at 295 K.

$$\mathbf{9} \xrightarrow{[Cr(CO)_5]} Cp'CpTa(CO)PMe_2Cr(CO)_5 \quad \mathbf{10}$$

Scheme 7

Table II. Spectroscopic data for $Cp'CpTa(CO)PMe_2Cr(CO)_5$ **10**.

Compounds		***10***
^{1}H NMR		
Cp		4.55 (d, J_{CpP} = 2 Hz, 5)
Cp′	CH	3.90 (s, br, 1)
		3.71 (s, br, 1)
	CH_3	1.88 (d, J_{PMe} = 1.7 Hz, 3)
		1.47 (s, 3)
	$C(CH_3)_3$	1.01 (s, 9)
PMe_2		1.84 (d, J_{PMe} = 5.1 Hz, 3)
		1.52 (d, J_{PMe} = 5.9 Hz, 3)
^{13}C NMR		
Cp		91.1
Cp′	ring	121.5, 105.8, 104.2, 90.2, 81.8
	CH_3	13.1, 12.7
	$C(CH_3)_3$	32.2
	$C(CH_3)_3$	31.8
PMe_2		28.0,25.6
Ta(CO)		254.0 (d, J_{CP} = 4 Hz)
cis-$Cr(CO)_4$		221.7 (d, J_{CP} = 10 Hz)
trans-Cr(CO)		224.7 (d, J_{CP} = 8 Hz)
^{31}P NMR		
PMe_2		−79.4
IR (THF)		
ν_{CO}		2 038 m, 1 938 s, 1 909 s

In C_6D_6 (295 K), ^{1}H and ^{13}C NMR (δ (ppm)/TMS), ^{31}P NMR (δ (ppm)/H_3PO_4).

In conclusion, we have described in this paper a chiral metalloligand which bears an asymmetric tantalum centre. This racemic metallophosphine is able to bind organometallic fragments to give chiral bimetallic complexes. Work to resolve the metallophosphine and to obtain pure enantiomeric forms of bimetallic derivatives is now underway.

Experimental section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents and eluents were dried and distilled under argon from sodium and benzophenone immediately before use. 3,4-dimethylcyclopent-2-enone **1** was prepared according to literature procedure [17]. Me_2PCl (Strem), *t*-BuLi (Aldrich), Bu_3SnCl (Aldrich) and $NaAlH_2(OCH_2CH_2OMe)_2$ (Aldrich) were used as received.

Elemental analyses (C, H) were performed by the Service central d'analyse du CNRS (Gif-sur-Yvette, France). Infrared spectra were recorded on a Nicolet 205 IR-FT. Mass spectra were recorded on a Kratos Concept 32 S spectrometer. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer; chemical shifts are given in ppm relative to Me_4Si (^{1}H, ^{13}C) or (external) H_3PO_4 (^{31}P).

Synthesis of $C_5H_3Me_2t$-Bu (Cp′H) **2**

To a stirred solution of *t*-BuLi (1.7 M in pentane, 100 mL, 0.17 mol), was added dropwise 15 g of **1** (0.136 mol) at −78 °C. The solution was allowed to warm to room temperature and stirred overnight. After this time, any remaining *t*-BuLi was hydrolyzed by slow, dropwise addition of methanol (6 mL) followed by water (15 mL). After decantation, the aqueous phase was extracted with ether (2 × 20 mL). The organic layer was washed with a solution prepared from ammonium chloride (2.3 g), concentrated hydrochloric acid (2 mL), and water (100 mL), until the aqueous phase became acidic. Then the organic solution was reduced to a volume of 50 mL on a rotary evaporator and vigorously stirred for 1.5 h with 2 mL of 6 M HCl solution, washed with a saturated sodium bicarbonate solution (2 × 10 mL) and then with water until neutral. The ethereal layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed by evaporation to give a yellow oil (16.3 g) which was used without purification for further synthesis. An analytically pure sample of **2** was obtained as a pale yellow oil by distillation: bp 38–39 °C/5 torr.

^{1}H NMR (C_6D_6, 200 MHz): δ 5.95 (s, 1, C*H*), 2.66 (s, 2, CH_2), 1.80 (s, 6, 2 CH_3), 1.13 (s, 9, *t*-Bu); ^{1}H NMR ($CDCl_3$): δ 5.90 (s, 1, C*H*), 2.84 (s, 2, CH_2), 1.88 (s, 3, CH_3), 1.81 (s, 3, CH_3), 1.13 (s, 9, *t*-Bu).

^{13}C {^{1}H} NMR (C_6D_6, 50 MHz): δ 155.4, 134.5, 132.8 (*C*, ring), 128.7 (*C*H), 44.2(CH_2), 33.4 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$), 13.6 (CH_3), 13.1 (CH_3).

Anal calc for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 86.18; H,11.81.

Synthesis of Cp′SnBu$_3$ **3**

To a stirred solution of 16.3 g of the unpurified oil **2** in 100 mL of pentane, 70 mL of MeLi 1.8 M in ether (0.126 mol) was added dropwise at 0 °C. The mixture was stirred at room temperature overnight. The resulting white powder was filtered, washed with pentane (3 × 20 mL), and dissolved in 100 mL of THF. 39 g of Bu_3SnCl (0.12 mol) was then added dropwise at 0 °C and the mixture was stirred at room temperature for 2 h. The solvent was then removed in vacuo. To the resulting thick yellow oil was added 60 mL of pentane, which caused the LiCl to precipitate. After filtration, the solid was extracted again with pentane (2 × 40 mL). The solvent was removed in vacuo from the combined solutions to give a yellow oil. **3** was obtained, as a pale yellow oil, by distillation over a 12 cm vigreux column. bp 100–105 °C/0.02 torr (32.4 g, yield from **1**, 54%).

^{1}H NMR (C_6D_6): δ 5.92 (s, 2, J(Sn–H) = 11 Hz, C*H*), 1.85 (s, 6, J(Sn–H) = 22.5 Hz, CH_3), 1.50 (m, 6), 1.7–1.3 (m, 6), 1.28 (s, 9, *t-Bu*), 0.92 (t, 9, ^3J(H–H) = 7.3 Hz), 0.85 (t, 6, ^3J(H–H) = 8.3 Hz).

^{13}C {^{1}H} NMR (C_6D_6): δ 146.9 (*C* ring, J(Sn–C) = 19 Hz), 116.9 (*C*H, J(Sn–C) = 8.5 Hz), 111.1 (*C* ring, J(Sn–C) = 43 Hz), 32.2 ($C(CH_3)_3$ J(Sn–C) = 5 Hz), 31.2 ($C(CH_3)_3$), 29.3 (CH_2, ^3J(Sn–C) = 19 Hz), 27.6 (CH_2, ^2J(Sn–C) = 61 Hz), 14.3 (CH_3), 13.7 (CH_3), ^4J(Sn–C) = 24 Hz), 10.8 (CH_2, ^1J(Sn–C) = 310 Hz).

MS (EI, 70 eV): *m/z* (fragment, rel intensity based on ^{120}Sn peaks) 440 (M^+, 41), 383 (M^+–Bu, 100), 291 (Bu_3Sn^+, 96), 269 (M^+–3Bu, 56), 235 (Bu_2SnH^+, 44), 179 ($BuSn^+$, 41), 149 (Cp'^+, 10).

Anal calc for $C_{23}H_{44}Sn$: C, 62.89; H, 10.10. Found: C, 62.79; H, 10.09.

Synthesis of Cp′TaCl$_4$ **4**

14.17 g of **3** (32.3 mmol) was added dropwise to a stirred suspension of 11.6 g of $TaCl_5$ (32.3 mmol) in 180 mL of pentane. After 24 h of stirring, the yellow suspension was filtered, washed with pentane (2 × 20 mL) and dried in vacuo to yield 13.1 g of **4** (85%).

^{1}H NMR (C_6D_6): δ 5.86 (s, 2, C*H*), 2.22 (s, 6, CH_3), 1.10 (s, 9, *t-Bu*).

^{13}C {^{1}H} NMR ($CDCl_3$): δ 152.4, 134.7, 118.7 (ring), 35.5 ($C(CH_3)_3$), 30.4 (C(CH_3)$_3$), 16.2 (CH_3).

Anal calc for $C_{11}H_{17}Cl_4Ta$: C, 27.99; H, 3.63. Found: C, 26.85; H, 3.46.

Synthesis of Cp' CpTaCl$_2$ **5**

Compound **5** was synthesized according to Bercaw's method reported for Cp*CpTaCl$_2$ [11] (Cp* = C_5Me_5) with minor modifications. 7.1 g of **4** (15 mmol) was reduced with 0.5 equiv of Mg in THF in the presence of 1 equiv of PMe_3. Removal of the solvent afforded a red residue. This crude product was treated with 1.32 g of CpNa (15 mmol) in toluene at 90 °C and the reaction monitored by ESR spectroscopy. After 3 h of stirring, extraction and crystallization in toluene afforded 3.4 g of green crystals of paramagnetic compound **5** (48%).

The ESR spectrum in toluene showed an eight-line spectrum: g_{iso} = 1.9270; $A_{Ta,iso}$ = 120.16 G.

Anal calc for $C_{16}H_{22}Cl_2Ta$: C, 41.22; H, 4.76. Found C, 41.07; H, 4.65.

Synthesis of Cp' CpTaH$_3$ **6**

3 g of **5** (6.4 mmol) was reduced by 5 mL of $NaAlH_2(OCH_2CH_2OMe)_2$ (2 M in toluene, 10 mmol) in 60 mL of toluene at 0 °C. After 3 h of stirring, the brown-red solution was hydrolyzed slowly by 10 mL of degassed water. The organic layer was decanted and extracted. Evaporation of the solvent, followed by recrystallization from toluene/pentane, afforded 1.77 g of white crystals of **6** (69%).

IR (nujol): ν_H 1 741, 1 761 cm^{-1}.

Anal calc for $C_{11}H_{17}Cl_4Ta$: C, 48.25; H, 6.33. Found: C, 47.05; H, 6.29.

Synthesis of Cp' CpTaH(CO) **7**

2 g of **6** was stirred in 30 mL of decane at 140 °C under carbon monoxide atmosphere for 3 h. The solvent was then removed under reduced pressure, and the residue was dried in vacuo. Sublimation at 110 °C and 0.02 torr afforded purple crystals of 1.8 g of **7** (85%).

IR (Nujol): ν_H 1 742 cm^{-1}, ν_{CO} 1 850 cm^{-1}.

Anal calc for $C_{17}H_{23}OTa$: C, 48.12; H, 5.46. Found: C, 47.96; H, 5.59.

Synthesis of [Cp' CpTa(CO)(PMe$_2$H)]Cl **8**

To a solution of 300 mg (0.71 mmol) of **7** in 20 mL of toluene was added one equiv of Me_2PCl. The pink precipitate was filtered, washed with toluene (5 mL) and pentane (2 × 10 mL), and dried in vacuo to yield 350 mg of **8** (95%).

Anal calc for $C_{19}H_{29}ClOPTa$: C, 43.82; H, 5.61. Found: C, 43.84; H, 5.65.

Synthesis of Cp' CpTa(CO)(PMe$_2$) **9**

To a solution of 250 mg (0.48 mmol) of metallophosphonium salt **8** in degassed water (10 mL), was added a saturated solution of potassium hydroxide (20 mL) followed by 20 mL of toluene. Then, the green organic layer was separated and the aqueous layer was extracted with toluene (20 mL). The solvent was removed and the green product was dried in vacuo to yield 210 mg of **9** (90%).

Anal calc for $C_{19}H_{28}OPTa$: C, 47.12; H, 5.83. Found: C, 46.66; H, 5.89.

Synthesis of Cp' CpTa(CO)(μ-PMe$_2$)Cr(CO)$_5$ **10**

To a solution of 150 mg (0.31 mmol) of **9** in 15 mL of THF was added an excess (20%) of $Cr(CO)_5$(THF) produced by irradiation of $Cr(CO)_6$. Then, the mixture was stirred for 45 min at room temperature. The solvent was removed in vacuo and the crude reaction product chromatographed on silica gel with toluene as eluent. Recrystallization from THF/pentane, afforded 150 mg of green crystals of **10** (72%).

Anal calc for $C_{24}H_{28}CrO_6PTa$: C, 42.62; H, 4.17. Found: C, 42.19; H, 4.38.

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