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Supplemental Information :

"Carbenes from Olefins ..." by Coalter, Spivak, Gérard, Clot, Eisenstein, and Caulton

Preparation of $RuHCl(P^iPr_3)_2$:

Under Ar, 1.00 g (2.18 mmol) of $RuH_2Cl_2(P^iPr_3)_2$ [1] and 0.321 g (2.18 mmol) of lithium 2,2,6,6-tetramethylpiperidide were added to a Schlenk flask equipped with a stir bar. Approximately 40 mL of benzene was added and the reaction allowed to stir 4-5 hours. The solvent was removed under vacuum and the solid residue was dried overnight *in vacuo*. The soluble products were extracted with pentane (ca. 3 times with 20 mL each). The pentane extracts were then combined and the solvent removed into a liquid N_2 trap. The reddish-brown crude product was the washed once with 10 mL of hexamethyldisiloxane and dried *in vacuo* to yield 0.665 g of $RuHCl(P^iPr_3)_2$ (72 %). ^1H NMR (400 MHz, C_6D_6, 20° C): δ -24.2 (t, $^2J_{P-H}$ = 32.8 Hz, Ru-*H*), δ 1.34 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 6.2 Hz, 18H, $P(CH\mathit{Me}_2)_3$), δ 1.36 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 6.2 Hz, 18H, $P(CH\mathit{Me}_2)_3$), δ 2.19 (m, 6H, $P(\mathit{C}H\mathrm{Mc}_2)_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 20° C): δ 84.1 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 20° C): δ 20.8 (s, $P(CH\mathit{Me}_2)_3$), δ 21.2 (s, $P(CH\mathit{Me}_2)_3$), δ 28.4 (vt, J_{P-C} = 6.4 Hz, $P(\mathit{C}H\mathrm{Me}_2)_3$).

Preparation and Analysis of $RuHCl(P^iPr_3)_2(=CMcOEt)$:

Under Ar, 25 mg (0.055 mmol) of $RuHCl(P^iPr_3)_2$ was placed in an NMR tube in C_6D_6. Via syringe, 5.2 μL, (0.055 mmol) of CH_2=CHOEt was added and the NMR tube capped. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra taken after approximately 30 minutes reveal quantitative conversion to $RuHCl(P^iPr_3)_2(=CMcOEt)$. ^1H NMR (300 MHz, C_6D_6, 20° C): δ -21.65 (t, $^2J_{P-H}$ = 22.8 Hz, 1H, Ru-*H*), δ 1.13 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 6.3 Hz, 18H, $P(CH\mathit{Me}_2)_3$), δ 1.25 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 6.3 Hz, 18H, $P(CH\mathit{Me}_2)_3$), δ 1.17 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, $Ru{=}CMcOCH_2C\mathit{H}_3$), δ 2.33-2.44 (m, 6H, $P(\mathit{C}H\mathrm{Mc}_2)_3$), δ 2.69 (s, 3H, $Ru{=}C\mathit{Me}OEt$), δ 4.37 (q, $^3J_{H-H}$ = 7.5 Hz, 2H, $Ru{=}CMcOC\mathit{H}_2CH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 20° C): δ 58.2 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 20° C): δ 14.6 (s, $Ru{=}CMcOCH_2(\mathit{C}H_3)$, δ 19.7 (s, $P(CH\mathit{Me}_2)_3$), δ 20.4 (s, $P(CH\mathit{Me}_2)_3$), δ 26.2 (vt, J_{P-C} = 9.1 Hz, $P(\mathit{C}H\mathrm{Mc}_2)_3$), δ 40.8 (s, $Ru{=}C\mathit{Me}OEt$), δ 68.5 (s, $Ru{=}CMcOCH_2CH_3$), δ 289.8 (t, $^2J_{P-C}$ = 9.7 Hz, $Ru{=}\mathit{C}McOEt$).

Upon cooling a sample of $RuHCl(P^iPr_3)_2(=CMcOEt)$ in toluene-d_8 to -90° C, slowed rotation of the ruthenium carbene bond gives rise to the decoalescence of the two isomers which differ in E/Z stereochemistry about the (X)(Y)Ru=CRR' bond. ^1H NMR (400 MHz, toluene-d_8, -80° C): New signals are seen at δ 4.95 and 4.29 (1:10 in population and coalesce to the time averaged signal at δ 4.38, $Ru{=}CMcOC\mathit{H}_2CH_3$), δ 2.06 and 2.87 (1:10 and coalesce at δ 2.68, $Ru{=}CMcOCH_2C\mathit{H}_3$), and δ -25.38 and -21.29 (1:10 and coalesce at δ -21.68, Ru-*H*). $^{31}P\{^1H\}$ NMR (162.0 MHz, toluene-d_8, -80° C): δ 51.8 and 56.4 (1:10 and coalesce at δ 56.0).

Reaction of $RuHCl(P^iPr_3)_2$ with CH_2=CHOEt - Detection of $RuHCl(P^iPr_3)_2(CH_2{=}CHOEt)$:

Under Ar, $RuHCl(P^iPr_3)_2$ (10 mg, 0.022 mmol) was dissolved in toluene-d_8 (ca. 0.5 mL) in an NMR tube equipped with a Teflon stopcock. The CH_2=CHOEt (2.0 μL, 0.022 mmol) was then added to the NMR tube such that it did not mix with the toluene-d_8 solution. The sample was then cooled in a dry-ice/isopropanol bath, shaken to thoroughly mix the reagents and placed immediately in a pre-cooled (-85° C) NMR spectrometer probe. The probe temperature was subsequently raised in 10° C increments (allowing 10 minutes to stabilize at each interval) and the ^1H and $^{31}P\{^1H\}$ spectra were recorded. Selected NMR spectroscopic data for $RuHCl(P^iPr_3)_2(CH_2{=}CHOEt)$: ^1H NMR (300 MHz,

toluene-d_8): δ -15.52 (t, $^2J_{P-H}$ = 17.7 Hz, 1H, Ru-*H*), δ 3.69 (m, 1H, Ru(CH_2=CHOC$H_2$$CH_3$)), δ 4.35 (m, 1H, Ru($CH_2$=CHOC$H_2$$CH_3$)), δ 2.02 (m, 3H, P(C*H*Me_2)$_3$), δ 2.32 (m, 3H, P(C*H*Me_2)$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8): δ 40.8, 46.0 (AB pattern, $^2J(P_A-P_B)$= 300 Hz).

Reaction of RuHCl(P^iPr_3)$_2$ with CH_2=CH_2 - Stable Adduct Formation :

Under Ar, 10 mg (0.022 mmol) RuHCl(P^iPr_3)$_2$ was added to an NMR tube equipped with a Teflon stopcock. The tube was filled with C_6D_6 to a predetermined mark on the tube so that the remaining head space volume was 4.0 mL. (approximately 0.5 mL C_6D_6). The NMR tube was cooled to zero degrees to freeze the benzene-d_6 and was then evacuated. It was then filled with CH_2=CH_2 to 95 mm Hg and the stopcock closed (0.022 mmol CH_2=CH_2). The tube was then warmed to room temperature, shaken, and its ^1H and $^{31}P\{^1H\}$ NMR spectra taken over 30 minute intervals. The stable adduct that formed showed little or no decomposition over a period of several hours. Spectroscopic data for RuHCl(P^iPr_3)$_2$(CH_2=CH_2) is as follows : ^1H NMR (400 MHz, C_6D_6, 20° C): δ -22.0 (t, $^2J_{P-H}$ = 18.0 Hz, Ru-*H*), δ 1.15 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.0 Hz, 18H, P(CH*Me*$_2$)$_3$), δ 1.20 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.0 Hz, 18H, P(CH*Me*$_2$)$_3$), 2.25 (m, 6H, P(C*H*Me_2)$_3$), δ 2.79 (t, $^4J_{P-H}$ = 3.2 Hz, 4H, Ru(CH_2=CH_2)). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 20° C): δ 44.1 (s).

Notes :

Preparation of CH_2=CDOEt :

The isotopically labeled olefin was prepared by hydrolysis of CH_2=C(Li)OEt with an excess of D_2O in o-xylene at -10° C. Filtration and fractional distillation (30-35° C fraction) of the resulting mixture yields 99% enriched CH_2=C(D)OEt. Preparation of the lithio salt, CH_2=C(Li)OEt is described in detail by Knorr, Rudolf, and Roman : *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 366-367.

Isolation of RuHCl(P^iPr_3)$_2$(=CMeOEt) :

The complex RuHCl(P^iPr_3)$_2$(=CMeOEt) can be isolated as a orange-brown viscous oil in a Schlenk flask from benzene if a larger quantity than can easily be generated *in situ* is required. No suitable wash solvent has been found as the complex is very soluble in most common organic solvents.

Preparation of RuDCl(P^iPr_3)$_2$:

Method 1 : Substitution of $RuD_2Cl_2(P^iPr_3)_2$ for its hydrido counterpart in the preparation above. $RuD_2Cl_2(P^iPr_3)_2$ was prepared with 99% enrichment by stirring $RuH_2Cl_2(P^iPr_3)_2$ under an atmosphere of D_2 in CH_2Cl_2 for 4 hours at 25° C. The headspace gases were removed and the flask refilled with D_2 once during this time period. The crude $RuD_2Cl_2(P^iPr_3)_2$ was then washed with ether and dried *in vacuo*.

Method 2 : RuDCl(P^iPr_3)$_2$ was prepared by stirring RuHCl(P^iPr_3)$_2$ in a small amount of acetone-d_6 for 12 hours at 25° C to allow isotopic exchange through the enol tautomer of the acetone-d_6.

Reference :

1. Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, 15, 1960-1962.