Supplementary Material for Chemical Communications

Supplementary data

A readily prepared neutral heterobimetallic titanium(IV)-rhodium(I) catalyst for intramolecular hydroacylation

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Supporting Information

Experimental Section

General. All manipulations were performed using standard Schlenk techniques. Deuterated dichloromethane was dried over activated 3A molecular sieves prior to use. All other chemicals were used as obtained from Strem or Aldrich Chemicals. The ligand $HOCMe_2CH_2PPh_2$, compound **10**, was synthesized according to literature procedures.[1] Compounds **1** and **8** were prepared and their hydroacylation behavior was monitored as previously described.[2] ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker

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[1] Ferguson, G. S.; Wolczanski, P. T.; *J. Am. Chem. Soc.* **1986**, *108*, 8293-8295.

[2] (a) Barnhardt, R. W.; Bosnich, B. *Organometallics* **1994**, *13*, 4131-4133. (b) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936-945.

DRX or AMX 400 instrument, and chemical shifts are reported in parts per million (ppm, δ) from Me_4Si (TMS, for ^1H), from residual solvent (CD_2Cl_2, δ 45.00 for ^{13}C), or from H_3PO_4 (for ^{31}P) standards. Mass spectra were recorded using fast atom bombardment (FAB) on a JEOL SX102a instrument.

In situ *preparation of (iPrO)Ti(μ: η^1, η^1-$OCMe_2CH_2PPh_2)_3RhCl$* (**14**). To a flame dried NMR tube equipped with Teflon stopcock was added $HOCMe_2CH_2PPh_2$ **10** (5.4 mg, 21 μmol, 3 eq.) in 0.5 mL CD_2Cl_2. Titanium tetraisopropoxide (2 mg, 7 μmol, 1 eq.) was subsequently added by microsyringe, resulting in an immediate color change from colorless to a pale yellow color ($^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): -23.38 ppm (s)). The solution was gently mixed for 0.5 hr. A solution of *bis*-(cyclooctadienerhodium(I) chloride) (2 mg, 4 μmol, 1.1 eq.) in CD_2Cl_2 (0.2 mL) was then added to the NMR tube, and the reaction mixture turned pale brown-yellow over the next 10 minutes. After 0.5 hr, the pentenal substrate (**1** or **8**, 70 μmol) was added via microsyringe to start the hydroacylation reaction. ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.81 (comp, 10H, Ph), 6.83 (comp, 20 H, Ph), 5.83 (d, J = 10 Hz, 1H), 5.47 (dd, J = 4, 10 Hz, 1H), 4.37 (s, 12H), 3.72 (m, J = 6 Hz, 1 H, iPr), 2.26 (d, J = 10 Hz, 1 H), 2.04 (br s, 2 H), 1.52 (comp, 2 H), 1.43 (s, 1H), 1.34 (comp, 3 H), 1.20 (s, 1 H), 1.06 (d, J = 6.4 Hz, 4 H), 0.97 (d, J = 6 Hz, 10 H, Me). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): 135.5, 134.5, 132.9, 132.3, 130.9, 130.8, 129.4, 129.3, 129.2, 128.6, 71.3, 41.9, 41.2, 32.0, 31.9, 28.6. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162.0 MHz): δ 18.194 (d, J_{RhP} = 147 Hz). Mass spectrum (FAB, m/z): 956.6 ($[M - O\textit{i}Pr]^+$), 877.6, 782.7, 652.8, 619.4, 455.3, 407.2, 275.3, 201.2, 132.9, 85.0, 41.0.

General Procedure for Rhodium(I)-diphosphine in situ *catalyst synthesis*. The following procedure is adapted from that reported by Sakai, et al.:[3] To a flame-dried NMR tube equipped with Teflon stopcock was added ligand (triphos, R-(+)-BINAP, *S*,*S*-(+)-DIOP, or *R*,*R*-(+)-BDPP: 35 μmol) in C_6D_6 or CD_2Cl_2 (0.5 mL). A solution of *bis*-(cyclooctadienerhodium(I) chloride) (3.2 mg, 3 μmol) in C_6D_6 or CD_2Cl_2 (0.2 mL) was added by flame-dried pipet. The reaction was sealed under nitrogen for 1 hour (a color change to orange yellow was noted, except for the triphos case, in which the reaction mixture instantaneously became yellowish brown). Substrate **1** (15 μmol) was then added by microsyringe to start the hydroacylation reaction.

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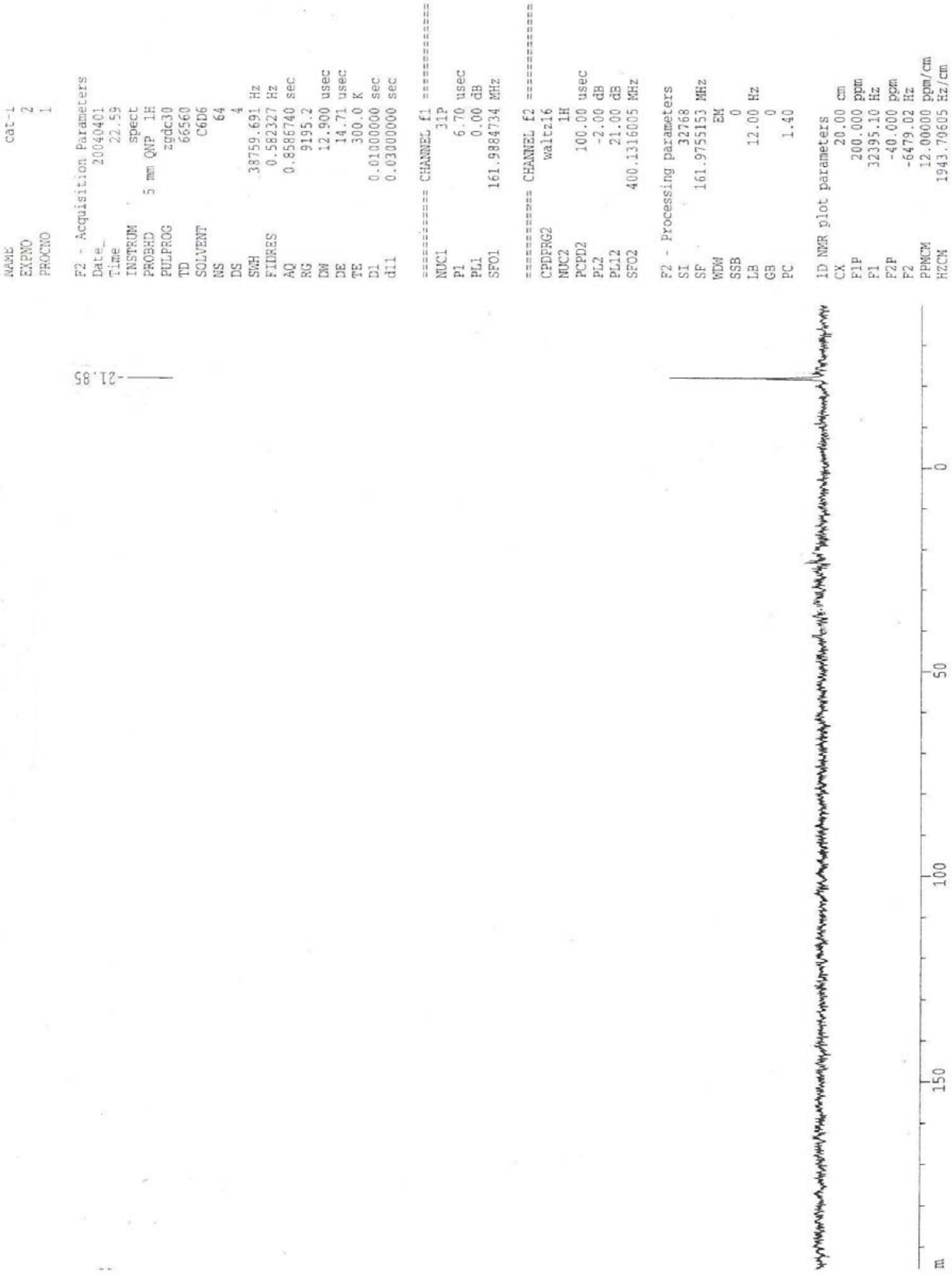
[3] Taura, Y.; Tanaka, M.; Wu, X. M.; Funakoshi, K.; Sakai, K. *Tetrahedron* **1991**, *47*, 4879-48888.

Compound 10, Ligand $HOCMe_2CH_2PPh_2$, ^{31}P NMR, 162 MHz, CD_2Cl_2.



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PROCNO            1

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TD            66560
SOLVENT        C6D6
NS               64
DS                4
SWH       38759.691 Hz
FIDRES     0.582327 Hz
AQ        0.8586740 sec
RG           9195.2
DW           12.900 usec
DE            14.71 usec
TE            300.0 K
D1       0.01000000 sec
d11      0.03000000 sec

============ CHANNEL f1 ============
NUC1            31P
P1             6.70 usec
PL1            0.00 dB
SFO1    161.9884734 MHz

============ CHANNEL f2 ============
CPDPRG2     waltz16
NUC2             1H
PCPD2        100.00 usec
PL2           -2.00 dB
PL12          21.00 dB
SFO2    400.1316005 MHz

F2 - Processing parameters
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WDW              EM
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GB                0
PC             1.40

1D NMR plot parameters
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F1P         200.000 ppm
F1         32395.10 Hz
F2P         -40.000 ppm
F2         -6479.02 Hz
PPMCM      12.00000 ppm/cm
HZCM     1943.70605 Hz/cm
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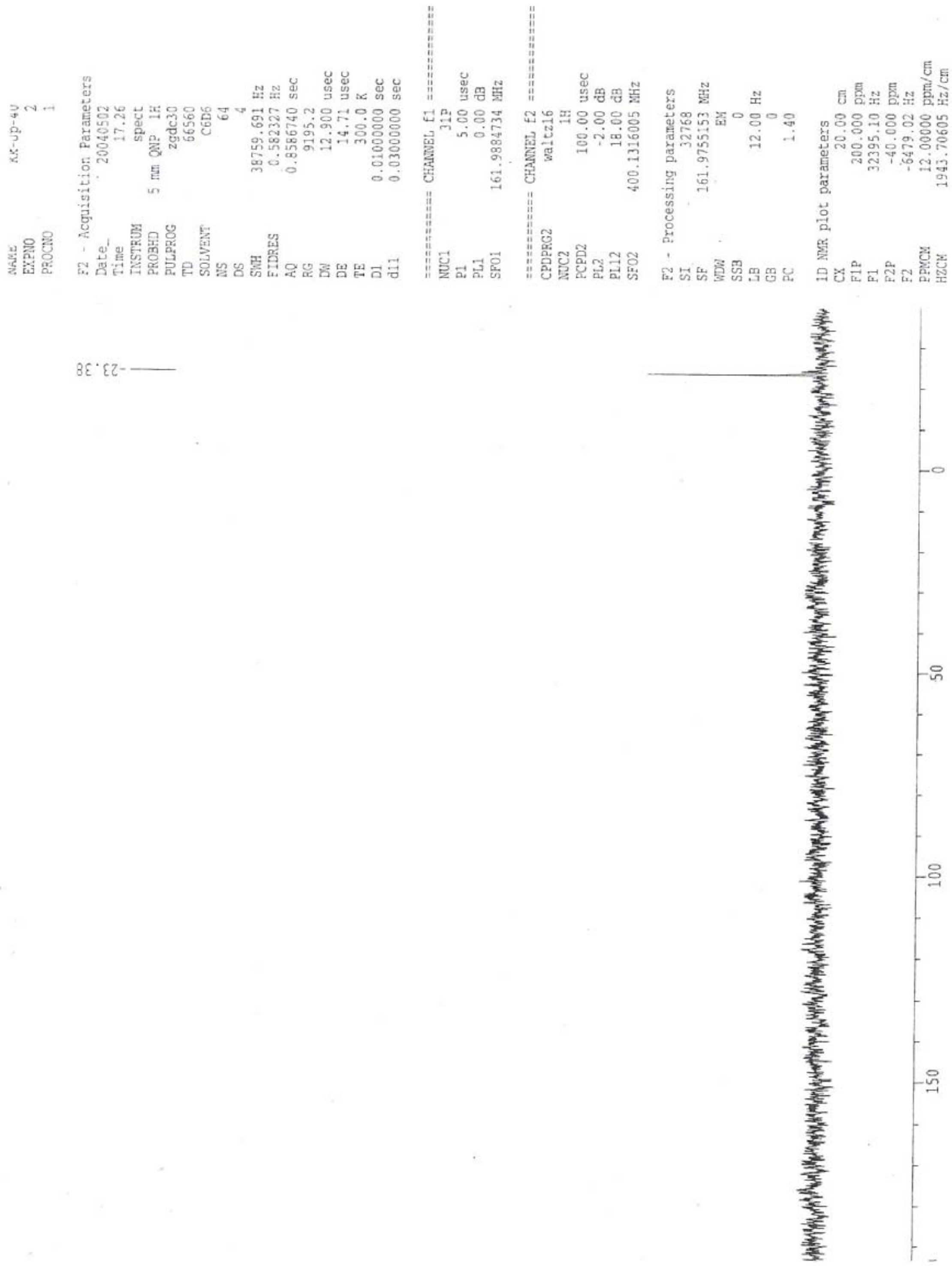
Supplementary Material for Chemical Communications

Compound 12, Ti(O*i*Pr)($OCMe_2CH_2PPh_2$)$_3$, ^{31}P NMR, 162 MHz, CD_2Cl_2.



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DS                      4
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FIDRES          0.582327 Hz
AQ             0.8586740 sec
RG                 9195.2
DW                 12.900 usec
DE                  14.71 usec
TE                  300.0 K
D1             0.01000000 sec
d11            0.03000000 sec

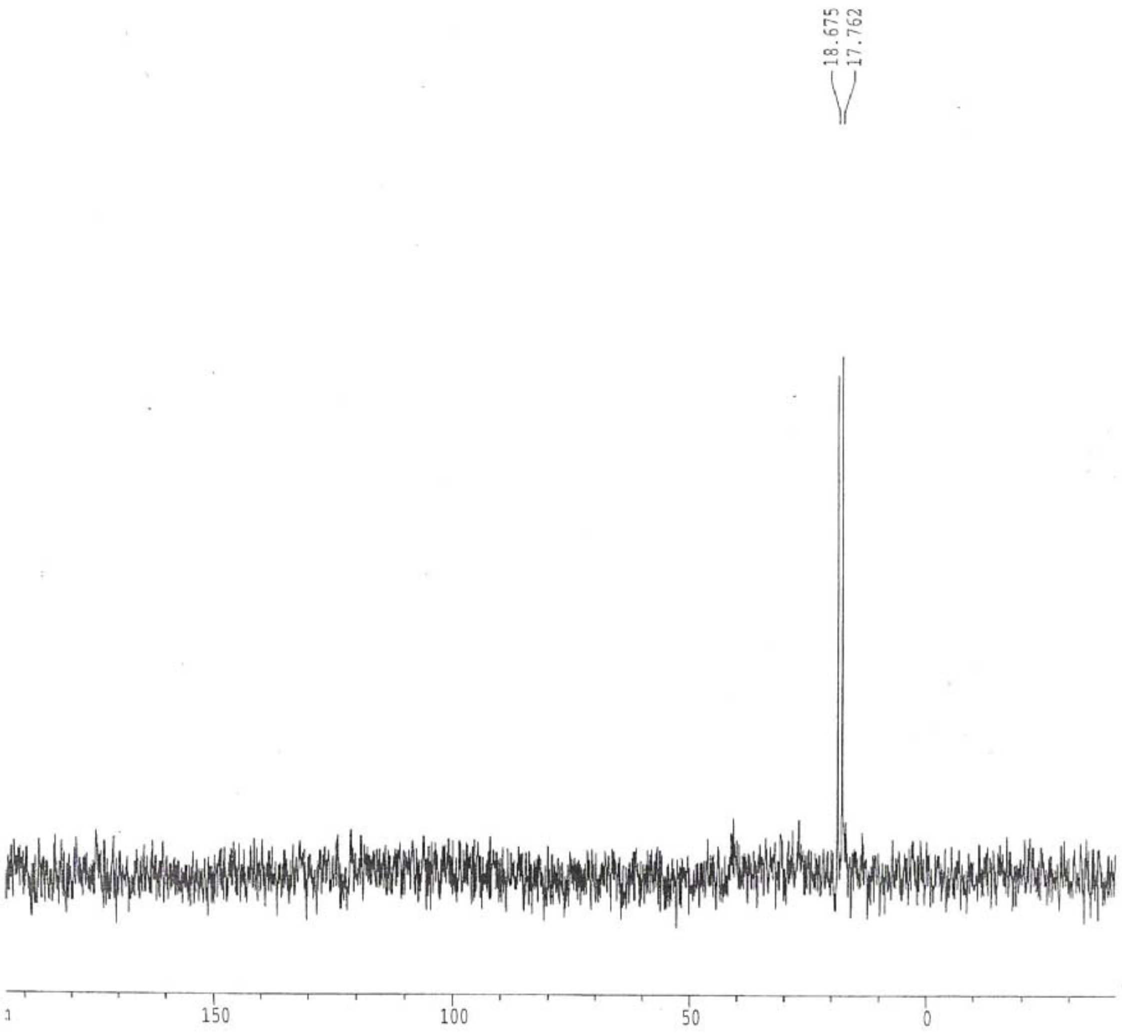
============ CHANNEL f1 ============
NUC1                  31P
P1                   5.00 usec
PL1                  0.00 dB
SFO1         161.9884734 MHz

============ CHANNEL f2 ============
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -2.00 dB
PL12                18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           161.9755153 MHz
WDW                    EM
SSB                     0
LB                  12.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               200.000 ppm
F1               32395.10 Hz
F2P               -40.000 ppm
F2               -6479.02 Hz
PPMCM            12.00000 ppm/cm
HZCM           1943.70605 Hz/cm
```

Compound 14, **(*i*PrO)Ti(μ:η^1,η^1-OCMe$_2$CH$_2$PPh$_2$)$_3$RhCl**, **^{31}P NMR, 162 MHz, CD$_2$Cl$_2$.**



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TD               66560
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NS                  64
DS                   4
SWH          38759.691 Hz
FIDRES        0.582327 Hz
AQ           0.8586740 sec
RG             14596.5
DW              12.900 usec
DE               14.71 usec
TE               300.0 K
D1          0.01000000 sec
d11         0.03000000 sec

============ CHANNEL f1 =============
NUC1               31P
P1                6.70 usec
PL1               0.00 dB
SFO1       161.9884734 MHz

============ CHANNEL f2 =============
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              -2.00 dB
PL12             21.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI               32768
SF         161.9755153 MHz
WDW                 EM
SSB                  0
LB               12.00 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
F1P            200.000 ppm
F1            32395.10 Hz
F2P            -40.000 ppm
F2            -6479.02 Hz
PPMCM         12.00000 ppm/cm
HZCM        1943.70605 Hz/cm
```

Oily solid which results from concentration of a dichloromethane solution of compound 14 under reduced pressure, ^{31}P NMR, 162 MHz, CD_2Cl_2.