Electronic Supporting Information

One-Step Synthesis and P–H Bond Cleavage Reactions of the Phosphanyl Complex *syn*-[MoCp{PH(2,4,6-C₆H₂^tBu₃)}(CO)₂] to Give Heterometallic Phosphinidene-Bridged Derivatives.

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Experimental Section

General Procedures and Starting Materials. All manipulations and reactions were carried out under an argon (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use.¹ Compounds PH₂R* (R* = 2,4,6-C₆H₂'Bu₃),² and [AuCl{P(p-tol)₃}],³ were prepared as described previously, and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338-343 K. Photochemical experiments were performed using Pyrex Schlenk tubes cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. A 400 W medium-pressure mercury lamp placed ca. 1 cm away from the Schlenk tube was used for these experiments. Purging of liberated CO in these experiments was done by bubbling N2 (99.9995%) through the solution. Filtrations were carried out through diatomaceous earth unless otherwise stated. Chromatographic separations were carried out using jacketed columns refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Commercial silica gel (230-400 mesh) and aluminum oxide (activity I, 70-290 mesh) were degassed under vacuum prior to use. The latter was mixed under argon with the appropriate amount of water to reach activity IV. IR stretching frequencies of CO ligands were measured in solution using CaF₂ windows, are referred to as ν (CO) and are given in wave numbers (cm⁻¹). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 298 K in CD₂Cl₂ solution unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (¹H, ¹³C) or external 85% aqueous H_3PO_4 solutions (³¹P). Coupling constants (J) are given in hertz. Yields of heterometallic derivatives of compound 1 (compounds 2 to 7) were based on the amount of compound 1 used in each preparation.

Preparation of *syn*-[MoCp(PHR*)(CO)₂] (1). A solution of [Mo₂Cp₂(CO)₆] (0.600 g, 1.22 mmol) and PH₂R* (0.342 g, 1.22 mmol) in toluene (10 mL) was irradiated with visible-UV light at 263 K for 4 h while gently bubbling N₂ (99.9995%), to give a dark purple solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/20) and the extracts were chromatographed on silica gel at 258 K. Elution with the same solvent mixture gave a blue-purple fraction yielding, after removal of solvents, compound **1** as a blue-purple solid (0.412 g, 68%). Anal. Calcd for C₂₅H₃₅MoO₂P: C, 60.73; H, 7.13. Found: C, 60.34; H, 7.28. ν(CO) (CH₂Cl₂): 1944 (vs), 1861 (s). ν(CO) (petroleum ether): 1958 (vs), 1888 (s). ν(CO) (MeCN): 1942 (vs), 1861 (s). ν(PH) (Nujol mull): 2275 (w). ³¹P{¹H} NMR (121.48 MHz, CD₂Cl₂): δ 272.7. ¹H NMR (300.13 MHz, CD₂Cl₂): δ 10.30 (d, *J*_{PH} = 339, 1H, PH), 7.40 [s, 2H, H³(C₆H₂)], 5.41 (s, 5H, Cp), 1.49 (s, 18H, *o*-^{*t*}Bu), 1.33 (s, 9H, *p*-^{*t*}Bu). ¹H NMR (300.13 MHz, C₆D₆): δ 10.20 (d, *J*_{PH} = 341, 1H,

PH), 7.45 [s, 2H, H³(C₆H₂)], 5.05 (s, 5H, Cp), 1.47 (s, 18H, *o*-^{*t*}Bu), 1.24 (s, 9H, *p*-^{*t*}Bu). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂): δ 242.1 (d, *J*_{CP} = 21, MoCO), 152.3 [s, C²(C₆H₂)], 152.2 [d, *J*_{CP} = 34, C¹(C₆H₂)], 142.7 [s, C⁴(C₆H₂)], 122.6 [d, *J*_{CP} = 7, C³(C₆H₂)], 95.4 (s, Cp), 38.7 [s, C¹(*o*-^{*t*}Bu)], 35.3 [s, C¹(*p*-^{*t*}Bu)], 33.3 [s, C²(*o*-^{*t*}Bu)], 31.3 [s, C²(*p*-^{*t*}Bu)].

Preparation of [MoReCp(μ -PR*)(CO)7] (2). A solution of compounds 1 (0.060 g, 0.121 mmol) and [Re₂(CO)₁₀] (0.080 g, 0.122 mmol) in toluene (8 mL) was irradiated with visible-UV light at 263 K for 20 min while gently bubbling N₂ (99.9995%), to give a brown-greenish solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/20) and the extracts were chromatographed on silica gel at 258 K. Elution with the same solvent mixture gave first a yellow fraction containing small amounts of uncharacterized species which was discarded, then a brown fraction, a black fraction, and finally a green fraction. Removal of solvents under vacuum from these fractions yielded respectively compounds 3 (brown solid, 0.008 g, 10%), the known complex $[Mo_2Cp_2(\mu-PR^*)(CO)_4]$ (black solid, 0.12 g, 13%), and compound 2 (green solid, 0.016 g, 16%). The crystals of 2 used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for C₃₀H₃₄MoO₇PRe: C, 43.96; H, 4.18. Found: C, 44.31; H, 4.01. v(CO) (CH₂Cl₂): 2135 (m), 2031 (vs), 2002 (m), 1905(w), 1820 (w). ³¹P{¹H} NMR (121.54 MHz, CD₂Cl₂): δ 437.6 (s, br). ¹H NMR (300.13 MHz, CD₂Cl₂): δ 7.34 [s, 2H, H³(C₆H₂)], 5.31 (s, 5H, Cp), 1.58 (s, 18H, o^{-t} Bu), 1.33 (s, 9H, p^{-t} Bu). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂): δ 249.3 (d, $J_{CP} = 15$, 2MoCO), 182.6 (s, br, 5ReCO), 165.0 [d, $J_{CP} = 50$, C¹(C₆H₂)], 149.0 [s, C⁴ (C_6H_2)], 148.1 [s, C²(C₆H₂)], 122.7 [d, $J_{CP} = 3$, C³(C₆H₂)], 95.3 (s, Cp), 39.7 [s, C¹(*o*-^tBu)], 35.4 [s, $C^2(o^{-t}Bu)$], 35.1 [s, $C^1(p^{-t}Bu)$], 31.3 [s, $C^2(p^{-t}Bu)$].

Preparation of [MoReCp(μ -PR*)(CO)₆] (3). A solution of compounds 1 (0.050 g, 0.101 mmol) and [Re₂(CO)₁₀] (0.066 g, 0.101 mmol) in toluene (8 mL) was irradiated with visible-UV light at 263 K for 15 min while gently bubbling N₂ (99.9995%), to give a brown-greenish solution which afterwards was stirred at 363 K for 25 min to give a brown solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/20) and the extracts were chromatographed on silica gel at 258 K. Elution with the same solvent mixture gave first a yellow fraction containing small amounts of uncharacterized species which was discarded, then a brown fraction, and finally a black fraction. Removal of solvents under vacuum from these fractions yielded respectively compounds **3** (brown solid, 0.020 g, 25%), and the known complex $[Mo_2Cp_2(\mu-PR^*)(CO)_4]$ (black solid, 0.05 g, 7%). Anal. Calcd for C₂₉H₃₄MoO₆PRe: C, 44.00; H, 4.33. Found: C, 43.71; H, 3.92. ν (CO) (CH₂Cl₂): 2077 (m), 1986 (vs), 1951(s), 1876 (w). ³¹P{¹H} NMR (121.54 MHz, CD₂Cl₂): δ 673.1 (s). ¹H NMR (300.13 MHz, CD₂Cl₂): δ 7.47 [s, 2H, $H^{3}(C_{6}H_{2})$], 5.09 (s, 5H, Cp), 1.43 (s, 18H, *o*-^{*t*}Bu), 1.39 (s, 9H, *p*-^{*t*}Bu). ¹³C{¹H} NMR (100.63) MHz, CD₂Cl₂): δ 231.7 (s, 2MoCO), 199.9 (d, J_{CP} = 37, ReCO), 191.9 (s, ReCO), 188.4 (d, $J_{CP} = 12$, 2ReCO), 152.5 [s, C⁴(C₆H₂)], 151.5 [s, C²(C₆H₂)], 150.3 [d, $J_{CP} = 28$, C¹(C₆H₂)], 123.0 [d, $J_{CP} = 7$, C³(C₆H₂)], 94.2 (s, Cp), 39.2 [s, C¹(*o*-*t*Bu)], 35.7 [s, C¹(*p*-*t*Bu)], 33.4 [s, C²(*o*-*t*Bu)], 31.4 [s, C²(*p*-*t*Bu)].

Preparation of [MoFeCp₂(\mu-PR*)(CO)₄] (4). BuLi (56 \muL of a 1.6 M solution in hexane, 0.090 mmol) was added to a tetrahydrofuran solution (8 mL) of compound 1 (0.040 g, 0.081 mmol) at 195 K, and the mixture was stirred for 1 min to give a dark green solution of Li[MoCp(PR*)(CO)₂]. This solution was then transferred rapidly using a canula into a Schlenk tube containing solid [FeCpI(CO)₂] (0.024 g, 0.079 mmol) kept at 195 K, and the mixture was then stirred at this temperature for 10 min to yield a brown solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/20) and the extracts were chromatographed on alumina at 258 K. Elution with the same solvent mixture gave a pink fraction containing small amounts of uncharacterized species, then a brown fraction yielding, after removal of solvents, compound 4 as a brown solid (0.030 g, 57%). This complex undergoes slow decarbonylation in dichloromethane solution at room temperature, to give complex 5. Anal. Calcd for C₃₂H₃₉FeMoO₄P: C, 57.33; H, 5.86. Found: C, 57.05; H, 5.47. Spectroscopic data for 4: v(CO) (CH₂Cl₂): 2027 (s), 1981 (s), 1901 (vs), 1817(s). ${}^{31}P{}^{1}H{}$ NMR (121.54 MHz, CD₂Cl₂): δ 477.6 (s). ${}^{1}H$ NMR (300.13) MHz, CD₂Cl₂): δ 7.38 [s, 2H, H³(C₆H₂)], 5.10, 5.04 (2s, 2 x 5H, Cp), 1.60 (s, 18H, *o*-^{*t*}Bu), 1.35 (s, 9H, *p*-^tBu). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂): δ 249.4 (d, *J*_{CP} = 15, MoCO), 213.6 (d, $J_{CP} = 16$, FeCO), 164.5 [d, $J_{CP} = 55$, $C^{1}(C_{6}H_{2})$], 149.1 [s, $C^{4}(C_{6}H_{2})$], 148.0 [s, $C^{2}(C_{6}H_{2})$], 123.1 [s, $C^{3}(C_{6}H_{2})$], 94.4 (s, MoCp), 88.3 (s, FeCp), 39.9 [s, $C^{1}(o^{-t}Bu)$], 35.8 [s, $C^{2}(o^{-t}Bu)$], 35.2 [s, $C^{1}(p^{-t}Bu)$], 31.1 [s, $C^{2}(p^{-t}Bu)$]. Spectroscopic data for $Li[MoCp(PR^*)(CO)_2]$: ³¹P{¹H} NMR (162.29 MHz, THF- d_8): δ 1009.5 (s, br). ¹H NMR (300.13 MHz, THF- d_8): δ 7.18 [s, 2H, H³(C₆H₂)], 4.87 (s, 5H, Cp), 1.37 (s, 9H, p-^tBu), 1.27 $(s, 18H, o^{-t}Bu).$

Preparation of [MoFeCp₂(µ-PR*)(CO)₃] (5). BuLi (70 µL of a 1.6 M solution in hexane, 0.112 mmol) was added to a tetrahydrofuran solution (8 mL) of compound 1 (0.050 g, 0.101 mmol) at 195 K, and the mixture was stirred for 1 min to give a dark green solution. Using a canula, this solution was rapidly transferred into a Schlenk tube containing solid [FeCpI(CO)₂] (0.035 g, 0.114 mmol) kept at 195 K, and the mixture was then stirred at this temperature for 10 min to yield a brown solution. This solution was transferred into a jacketed Schlenk tube, then irradiated with visible-UV light at 288 K for 15 min while keeping a gentle N₂ (99.9995%) purge. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/20) and the extracts were chromatographed on silica gel at 258 K. Elution with dichloromethane/petroleum ether (1/1) gave a brown fraction yielding, after removal of solvents, compound 5 as a brown solid (0.040 g, 62%). Anal. Calcd for C₃₂H₄₁Cl₂FeMoO₃P (5·CH₂Cl₂): C, 52.84; H, 5.68. Found: C, 52.82 H, 6.43. ν (CO) (CH₂Cl₂): 1945 (m), 1910 (vs), 1770 (m, sh), 1747 (m). ³¹P{¹H} NMR (121.54 MHz, CD₂Cl₂): δ 674.0 (s). ¹H NMR (300.13 MHz, CD₂Cl₂): δ 7.48 [s, 2H, H³(C₆H₂)], 5.23, 4.51 (2s, 2 x 5H, Cp), 1.64, 1.47 (2s, br, 2 x 9H, *o*-*t*Bu), 1.38 (s, 9H, *p*-*t*Bu). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂): δ 258.0, 254.2 (2s, MoCO), 219.9 (d, *J*_{CP} = 16, FeCO), 153.6, 152.6 [2s, br, C²(C₆H₂)], 152.8 [s, C⁴(C₆H₂)], 151.0 [d, *J*_{CP} = 45, C¹(C₆H₂)], 123.6, 123.3 [2s, br, C³(C₆H₂)], 94.4 (s, MoCp), 85.4 (s, FeCp), 39.2 [s, 2C¹(*o*-*t*Bu)], 35.7 [s, C¹(*p*-*t*Bu)], 33.9, 32.9 [2s, br, C²(*o*-*t*Bu)], 31.3 [s, C²(*p*-*t*Bu)].

Preparation of [MoAuCp(µ-PR*)(CO)₂{P(*p***-tol)₃}] (7). Sodium amalgam (ca. 0.5 mL of a** 0.5% amalgam, ca. 1.5 mmol) was added to an acetonitrile solution (8 mL) of compound 1 (0.050 g, 0.101 mmol) at 243 K, and the mixture was stirred for 5 min to give a dark green solution of the paramagnetic complex Na[MoCp(PHR*)(CO)₂], identified by C–O stretching bands at 1858 (vs) and 1760 (s) cm⁻¹. Using a canula, this solution was rapidly transferred into a Schlenk tube containing solid [AuCl{P(p-tol)₃}] (0.054 g, 0.101 mmol) kept at 243 K, and the mixture was stirred at this temperature for 20 min, then allowed to reach room temperature for 20 min to give a dark green solution. The solvent was then removed under vacuum, the residue was washed with petroleum ether, then extracted with dichloromethane/petroleum ether (1/20), and the extracts were chromatographed on alumina at 258 K. Elution with the same solvent mixture gave first a blue fraction containing significant amounts of the parent compound 1, then a yellow-green fraction containing small amounts of uncharacterized species which was discarded, and finally a green-blue fraction yielding, after removal of solvents, compound 7 as a green solid (0.030 g, 30%). Anal. Calcd for C₄₆H₅₅AuMoO₂P₂: C, 55.54; H, 5.57. Found: C, 55.20; H, 5.15. v(CO) (CH₂Cl₂): 1904 (vs), 1817 (s). ³¹P{¹H} NMR (121.54 MHz, CD₂Cl₂): δ 528. 4 (d, $J_{PP} = 275$, μ -PR*), 38.6 (d, $J_{\rm PP} = 275$, AuP). ¹H NMR (300.13 MHz, CD₂Cl₂): δ 7.46 [m, 6H, H²(C₆H₄)], 7.36 [s, 2H, $H^{3}(C_{6}H_{2})$], 7.29 [d, $J_{HH}=7$, 6H, $H^{3}(C_{6}H_{4})$], 5.16 (s, 5H, Cp), 2.40 (s, 9H, Me), 1.56 (s, 18H, o-^tBu), 1.35 (s, 9H, *p*-^tBu). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂): δ 248.3 (d, *J*_{CP} = 16, MoCO), 148.8 [s, C⁴(C₆H₂)], 148.6 [s, C²(C₆H₂)], 142.6 [s, C⁴(C₆H₄)], 134.5 [d, $J_{CP} = 14$, $C^{2}(C_{6}H_{4})$], 130.3 [d, $J_{CP} = 12$, $C^{3}(C_{6}H_{4})$], 127.2 [d, $J_{CP} = 50$, $C^{1}(C_{6}H_{4})$], 122.0 [s, $C^{3}(C_{6}H_{2})$], 94.9 (s, Cp), 39.1 [s, $C^{1}(o^{-t}Bu)$], 35.1 [s, $C^{1}(p^{-t}Bu)$], 34.8 [s, $C^{2}(o^{-t}Bu)$], 31.4 [s, $C^{2}(p^{-t}Bu)$], 21.6 (s, Me). The resonance of the $C^{1}(C_{6}H_{2})$ atom could not be located in the spectrum.

X-Ray Structure Determination of Compound 2. Diffraction data were collected at 150 K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu K α radiation. Images were collected at a 62 mm fixed crystal-detector distance using the oscillation method, with 1° oscillation and variable exposure time per image (5-15 s). Data collection strategy was calculated with the program *CrysAlis Pro CCD*,⁴ and data reduction and cell refinement was performed with the program *CrysAlis Pro RED*.⁴ An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program *CrysAlis Pro RED*. Using the program suite WINGX,⁵ the structure was solved by Patterson interpretation and phase expansion using SHELXL2016, and refined with full-matrix least

squares on F^2 using SHELXL2016.⁶ All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically placed and refined using a riding model to give the residuals shown in Table S1.

	2
mol formula	C ₃₀ H ₃₄ MoO ₇ PRe
mol wt	819.69
cryst syst	Triclinic
space group	<i>P</i> -1
radiation (λ , Å)	1.54184
<i>a</i> , Å	10.3435(3)
b, Å	10.6128(3)
<i>c</i> , Å	14.9254(4)
α , deg	74.056(3)
β , deg	81.568(3)
γ, deg	82.695(3)
V, Å ³	1551.84(8)
Z	2
calcd density, g cm ⁻³	1.754
absorp coeff, mm ⁻¹	11.667
temperature, K	149.8(2)
θ range (deg)	4.34-69.50
index ranges (h, k, l)	-12, 11; -12, 12; -15, 17
no. of reflns collected	13329
no. of indep reflns (R_{int})	5583(0.0380)
refines with $I > 2\sigma(I)$	5125
<i>R</i> indexes [data with $I > 2\sigma(I)$] ^{<i>a</i>}	$R_1 = 0.0234; wR_2 = 0.0621$
R indexes (all data) ^{a}	$R_1 = 0.0276; wR_2 = 0.0763$
GOF	1.126
no. of restraints/params	0 / 370
$\Delta \rho$ (max., min.), eÅ ⁻³	0.805 / - 0.860
CCDC deposition no	1908717

Table S1. Crystal Data for Compound 2

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. wR = [\Sigma w(|F_{o}|^{2} - |F_{c}|^{2})^{2} / \Sigma w |F_{o}|^{2}]^{1/2}. w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP] \text{ where } P = (F_{o}^{2} + 2F_{c}^{2})/3. {}^{b}a = 0.0436, b = 0.0000.$

Computational Details. All DFT calculations were carried out using the GAUSSIAN09 package,⁷ in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional,⁸ and the Lee-Yang-Parr correlation functional.⁹ An accurate numerical integration grid (99,590) was used for all the calculations *via* the keyword Int=Ultrafine. Effective core potentials and their associated double- ζ LANL2DZ basis set were used for Mo atoms.¹⁰ The light elements (P, O, C and H) were described with the 6-31G* basis.¹¹ Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of related species. Frequency analyses were performed for all the stationary points to ensure that minimum structures with no imaginary frequencies were achieved.

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Figure S1. B3LYP-DFT-optimized structures of compounds 1, *anti*-1 and anion 6, with most H atoms and 'Bu groups (except their C^1 atoms) omitted.

Parameter	1	anti-1	6
Mo-P	2.271	2.273	2.417
P–C	1.857	1.854	1.895
P–H	1.418	1.421	1.420
Мо-СО	1.977	1.977	1.944
	1.978	1.979	1.955
Mo-P-H	125.3	120.2	121.6
Мо-Р-С	131.8	135.3	119.4
H–P–C	102.9	104.4	101.9
$\Sigma(X-P-Y)$	360.0	359.9	342.9
OC-Mo-CO	82.0	80.8	83.9

 Table S2. Selected bond lengths (Å) and angles (°) for 1, anti-1 and anion 6.

Table S3. DFT/B3LYP-calculated wavenumbers $v(cm^{-1})$ and relative intensities of the P–H and C–O stretches for **1**, *anti*-**1** and anion **6**.

	<i>v</i> (Р–Н)	v(C-O)
1	2408 (6)	2047 (100), 1996 (71)
anti-1	2389 (10)	2043 (90), 1989 (100)
6	2384 (9)	1949 (100), 1890 (74)



Figure S2. B3LYP-DFT-computed spin density for anion 6

Table S4. Mulliken atomic spin densities for anion 6

1	Mo	0.549675
2	С	0.025211
3	0	0.028270
4	С	0.008561
5	0	0.017938
6	С	0.018329
7	Η	-0.001104
8	C	-0.013404
9	Η	0.000694
10	С	-0.017346
11	Η	0.000899
12	С	0.079185
13	Η	-0.004310
14	С	-0.014626
15	Η	0.000491
16	Р	0.290702
17	С	0.008686
18	С	-0.001211
19	С	0.000923
20	Η	-0.000181
21	С	-0.001617
22	С	0.001824
23	Η	0.001044
24	С	0.003624

25 C	0.000918
26 C	0.010569
27 H	0.001528
28 H	0.000146
29 H	0.000466
30 C	0.001608
31 H	0.000450
32 H	0.000317
33 H	-0.002398
34 C	0.000321
35 H	0.000040
36 H	0.000001
37 H	0.000195
38 C	0.000091
39 C	-0.000037
40 H	0.000001
41 H	-0.000003
42 H	-0.000018
43 C	-0.000043
44 H	-0.000017
45 H	0.000002
46 H	0.000000
47 C	0.000012
48 H	0.000007

49 H 0.000047 50 H -0.000007 51 C -0.000114 52 C 0.000023 53 H -0.000054 54 H -0.000040 55 H -0.000010 56 C 0.001121 57 H 0.000006 58 H -0.000618 59 H 0.001147 60 C 0.000215 61 H -0.000065 62 H -0.000082 63 H 0.000007 64 H 0.002012 Sum of spin densities = 1.00000

NMR SPECTRA FOR NEW COMPLEXES



 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture in the preparation of compound 1 (CH_2Cl_2)



¹¹H NMR spectrum of compound **1** (CD₂Cl₂)





 $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of compound **3** (CD_2Cl_2) (δ_{P} = 673.1 ppm)





 ^1H NMR spectrum of the crude reaction mixture in the preparation of $Li[MoCp(PR^*)(CO)_2]$ (THF-d_8)



800 780 760 740 720 700 680 660 640 620 600 580 560 540 520 500 480 460 440 420 400 380 360 340 320 300 280 260 240 220 200 f1 (ppm)

 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture in the preparation of compound 4 (CH_2Cl_2)



¹H NMR spectrum of compound **4** (CD_2Cl_2). Resonances marked * belong to compound **5** (see text).



 $^{31}P{^{1}H}$ NMR spectrum of the crude reaction mixture in the preparation of compound **5** (CH₂Cl₂)





 $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture in the preparation of compound 7 (CH_2Cl_2, low-field region)



 $^{31}P\{^{1}H\}$ NMR spectrum of compound **7** (CD₂Cl₂, low-field region)





¹H NMR spectrum of compound **7** (CD₂Cl₂)