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Group 6 Metal Carbonyl Complexes Supported by a Bidentate PN Ligand: Syntheses, Characterization, and Catalytic Hydrogenation Activity

Thomas Vielhaber, Kirill Faust, and Christoph Topf*

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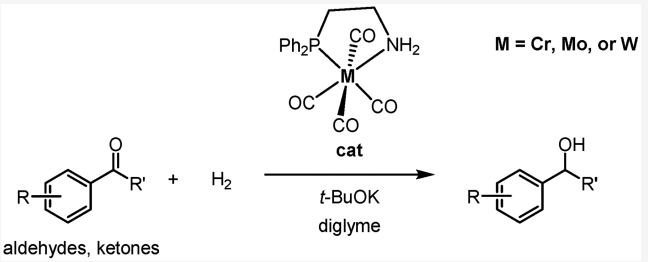
ABSTRACT: We report on the preparation of a series of phosphorus−nitrogen donor ligand complexes $[M(CO)_4(PN)]$, where M = Cr, Mo, W and PN is 2-(diphenylphosphino)-ethylamine. The organometallic compounds were readily obtained upon reacting the respective metal hexacarbonyls with equimolar amounts of the pertinent ligand in the presence of tetraethylammonium bromide. The PN-ligated metal carbonyls were fully characterized by standard spectroscopic techniques and X-ray crystallography. The ability of the title compounds to function as homogeneous hydrogenation catalysts was probed in the reduction of acetophenone and benzaldehyde derivatives to yield the corresponding alcohols. The reaction setup was easily assembled by simply combining the components in the autoclave on the bench outside an inert-gas-operated glovebox system.



INTRODUCTION

The past decade has witnessed tremendous progress in the syntheses of first row transition metal pincer complexes and their catalytic applications in a variety of (de)hydrogenation reactions.[1] In this context, PNP-ligated metal atoms and ions have played a dominant role by virtue of their intrinsically well balanced stability−reactivity relationship and the synthetic malleability of the given tridentate ligand. Driven by economic considerations, the related scientific discourse was, to a great degree, centered around the use of base metals as catalytically competent centers.[2] Among the latter, manganese represents an attractive candidate owing to its good abundance, low price, excellent biocompatibility, and rich coordination chemistry.[3] Indeed, the first report on a PNP-tagged manganese carbonyl hydrogenation catalyst[4] stimulated a rapid and impressive development in the field[5] which will unequivocally continue to excel in the future.

However, in 2017 Pidko and co-workers demonstrated that the capability of tridentate PNP ligand−manganese assemblies carries over to a congeneric but more truncated PN-based Mn complex that effects the hydrogenation of esters in the presence of substoichiometric amounts of *t*-BuOK.[6] The respective catalyst is prepared by reacting the commercial but notoriously expensive $[Mn(CO)_5Br]$[7] with an equimolar amount of 2-(diphenylphosphino)ethylamine. Furthermore, Sortais, Bastin, and their co-workers devised a method for the asymmetric transfer hydrogenation of ketones using chiral aminophosphines and the aforementioned manganese precursor.[8] This recent reports and the ongoing pursuit of cost-effective catalytic protocols encouraged us to embark on a study toward the syntheses of group 6 metal complexes incorporating the anionic $[M(CO)_3(PN)Br]^-$ motif (M = Cr, Mo, W). We anticipated this coordination unit to faithfully reproduce the catalytic properties of the privileged manganese-based congener mentioned above, while the preparation of the pertinent compounds follows the rational guidelines as outlined in the literature. The respective precursor salts $[M(CO)_5Br][NEt_4]$ are easily obtained upon decarbonylation of the respective readily available metal hexacarbonyls with tetrabutylammonium bromide in refluxing glyme or diglyme[9] (vide infra), whereupon the notional catalysts $[M(CO)_3(PN)Br][NEt_4]$ are obtained through ligand exchange reaction of 2 equiv of CO effected by the given bidentate PN ligand (Scheme 1). Since the ability of the vast majority of PNP- and PN-tagged metal carbonyls to cleave gaseous H_2 depends on the presence of a deprotonatable metal-bound NH motif, pairing complexes $[M(CO)_3(PN)Br][NEt_4]$ with a strong and soluble base (e.g., *t*-BuOK or *t*-BuONa) is thought to give rise to a hydrogenation catalyst assembly.

It is worth noting that, while the coordination chemistry and catalytic applications of chromium,[10] molybdenum,[11] and tungsten[11] complexes featuring a PNP backbone have already been extensively described and are partially very well

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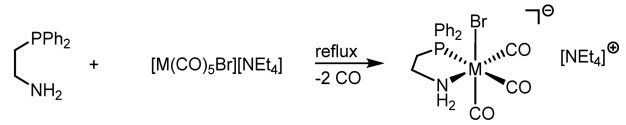
Scheme 1. (A) General Synthesis of Ionic Bromo Pentacarbonyl Precursors $[M(CO)_5Br][NEt_4]$ from Commercial Carbonyls $[M(CO)_6]$ and Cheap Tetrabutylammonium Bromide and (B) Formation of Notional Catalysts $[M(CO)_3(PN)Br][NEt_4]$ Thereof upon CO Extrusion Effected by 2-(Diphenylphosphino)ethylamine (M = Cr, Mo, W)[a]

A.

B.



[a]Dry glyme is a proper solvent for both reactions.

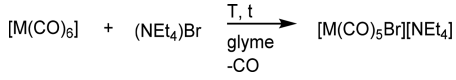
developed, related reports on PN-liganded kindred[12] have been hitherto almost unknown (vide infra).

RESULTS AND DISCUSSION

Initially, we prepared a series of group 6 metal based starting materials of the general formula $[M(CO)_5Br][NEt_4]$ (M = Cr, Mo, W) featuring an anionic metal carbonyl fragment which is isoelectronic with the frequently used but high-priced manganese-based precursor compound $[Mn(CO)_5Br]$ (vide supra). The original literature method for the syntheses of the pertinent bromopentacarbonyl metal salts relied on the use of diglyme as the solvent,[9] but we soon realized that its high viscosity compromises the agitation of the reaction mixture and residues of this solvent persistently stuck on the synthesized compounds owing to the rather high boiling point (162 °C)[13] of the former, which requires annoyingly prolonged drying periods on the vacuum pump. Accordingly, we replaced this solvent with the more volatile but still sufficiently well coordinating glyme, the boiling point of which is 84 °C,[13] and worked out an optimized reaction parameter set for each goup 6 metal carbonyl (Table 1).

With pristine samples of the precursors $[M(CO)_5Br][NEt_4]$ in hand, we went straight away to assemble the projected catalysts via reaction of the former with 2-(diphenylphosphino)ethylamine (Scheme 1B). Surprisingly, soon after starting the complex-generating reaction we noticed the appearance of a colorless microcrystalline precipitate which indicated back-formation of solid $(NEt_4)Br$. The latter was filtered off, and thereafter a small amount of silver(I) nitrate was added to the clear filtrate. Indeed, the addition of $AgNO_3$ did not produce a precipitate of insoluble AgBr, and thus we had to infer that the prepared PN complex did not contain any bromide ligand. Finally, IR spectroscopy and X-ray crystallography delivered certainty about the actual constitution of the PN-ligated metal complexes (Figure 1). It turned out that refluxing a mixture of $[M(CO)_5Br][NEt_4]$ and the given bidentate ligand solely resulted in the formation of the PN-tagged tetracarbonyl complexes $[M(CO)_4(PN)]$ (M = Cr (**1**), Mo (**2**), W (**3**)) (Scheme 2).

Table 1. General Reaction Scheme for the Preparation of the Requisite Precursor Salts Incorporating the Anionic Coordination Unit $[M(CO)_5Br]^-$ (M = Cr, Mo, W) along with Optimized Reaction Conditions and Optical Appearance of the Products[a]



central metal M	reaction temp T (°C)	reaction time t (min)	yield (%)
Cr	120	90	84 (orange crystalline powder)
Mo	80	150	77 (yellow crystalline powder)
W	130	80	82 (yellow crystalline powder)

[a]Each reaction was performed with 0.68 mmol of the corresponding $[M(CO)_6]$ starting material.

In order to deliberately synthesize the corresponding ionic bromido pentacarbonyl metalate, the reaction was performed under reduced pressure with the intention to provide thermodynamic bias for CO extrusion from the metal core while at the same time the dissociation of the bromido ligand was intended to be suppressed. However, we again exclusively obtained the neutral carbonyl complexes $[M(CO)_4(PN)]$ (M = Cr, Mo, W) and never observed formation of the pursued ionic species.

In the interest of saving time, we then devised a convenient in situ method which dispenses with the need for an extra isolation step of the salts $[M(CO)_5Br][NEt_4]$ and which therefore allows for a quicker access to the PN ligand supported notional catalysts. For the molybdenum compound, the synthesis of the pertinent PN complex also succeeds with the corresponding BF_4 salt of the given PN ligand, i.e. 2-(diphenylphosphino)ethylammonium tetrafluoroborate, provided that stoichiometric amounts of a mild base (triethylamine) are present in the reaction mixture. This is of particular practical interest, since the aforementioned PN-BF_4 salt is an easy to weigh solid, whereas the parent PN compound is a very viscous oil that is not as readily portionable.

Related reports on the preparation and characterization of group 6 metal chelates that incorporate tertiary amine or pyridine based donor motifs[14] already exist, but to the best of our knowledge, other than mechanistic studies of their ring-opening reactions,[15] further accounts dealing with the reactivity of generic complexes $[M(CO)_4(PN)]$ have not yet been composed.

However, on adopting the literature protocol[16] that describes the direct reaction of the respective metal hexacarbonyls $[M(CO)_6]$ (M = Cr, Mo, and W) with an equimolar amount of the bidentate PN ligand, we soon realized that application of the congeneric PN-BF_4 salt does not work for this particular synthesis of the chromium and tungsten derivatives, most probably owing to the fact that the given salt is almost insoluble in nonpolar solvents. Accordingly, we followed the same protocol as outlined in the literature[16] and applied the free PN ligand as well. Finally, we obtained the desired complexes as yellow crystalline powders in very good yields and the thus-prepared coordination compounds were characterized by infrared spectroscopy, as already described in the report from Walsh et al.,[16] and additionally by us through X-ray crystallography, high-resolution mass spectrometry, and ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

It is worth noting that the temperature for the CO extrusion is significantly lowered if the syntheses of complexes **1**−**3** proceed via the respective intermittently generated $[M(CO)_5Br][NEt_4]$ species (see the Experimental Section for details).

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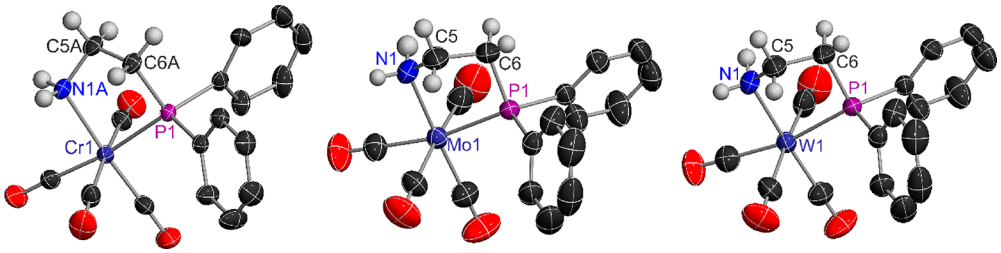
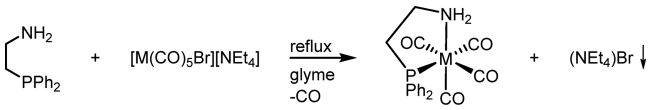


Figure 1. ORTEP drawings of the prepared carbonyl complexes $[M(CO)_4(PN)]$, M = Cr, Mo, W. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 2. Actual Reaction Outcome on Combining 2-(Diphenylphosphino)ethylamine and Ionic Group 6 Metal Carbonyl Compounds $[M(CO)_5Br][NEt_4]$ in Refluxing Glyme[a]

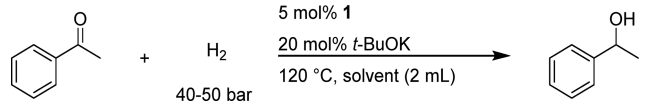


1 - 3

[a]The reaction exclusively produced the bromide-free complexes $[M(CO)_4(PN)]$ (M = Cr (**1**), Mo (**2**), W (**3**)).

Catalytic Hydrogenation Reactions of Carbonyl Derivatives with $[Cr(CO)_4(PN)]$ (1). In initial hydrogenation experiments we tested PN-tagged complex **1** for its ability to catalyze the reduction of ketones. We chose acetophenone as the benchmark substrate and probed the catalytic performance in different solvents (Table 2) while the catalytic reactions were performed in the presence of excess *t*-BuOK versus the catalyst. To our delight, complex **1** showed considerable catalytic activity at 120 °C and 40−50 bar of H_2 pressure, provided the reaction was performed in coordinating solvents.

Table 2. Catalytic Hydrogenation of Acetophenone to Afford 1-Phenylethanol Facilitated by the Neutral Carbonyl Complex $[Cr(CO)_4(PN)]$ (1) in Different Solvents and in the Presence of *t*-BuOK[a]



entry	solvent	reaction time (h)	*p* (bar)	conversion (%)	yield (%)
1	cyclohexane	24	50	0	0
2	*n*-heptane	24	50	0	0
3	toluene	24	50	0	0
4	isopropyl ether	24	50	0	0
5	tetrahydrofuran	24	50	48	48
6	1,4-dioxane	24	50	44	44
7	glyme	22	50	>99	90
8	diglyme	22	50	>99	99
9	glyme	18	40	45	34
10	diglyme	18	40	>99	99
11	acetonitrile	24	50	>99	34
12	dimethylformamide	18	40	>99	65
13	pyridine	18	40	35	10

[a]A 0.5 mmol amount of acetophenone was used. Conversions and yields were determined by GC-MS analysis using *n*-dodecane as the internal standard.

In stark contrast to this, the activity completely ceased in nonpolar solvents (entries 1−3) and when isopropyl ether was used as the reaction medium the steric bulk of the alkyl groups in the solvent also seemed to fully inhibit the catalytic transformation (entry 4). Strikingly, upon a change in the solvent from glyme to diglyme, the catalytic performance was drastically increased and the substrate was fully converted to the desired product with nearly quantitative yield after 18 h (entries 9 and 10). This trend is clearly a result of the ability of diglyme to effectively solubilize the potassium alcoholate by providing three contiguous and regularly spaced oxygen donor atoms to the K^+ ions. We also observed complete conversion for dimethylformamide and acetonitrile as solvents, but the yields were rather poor owing to the formation of side products, which escaped detection through the GC-MS device. Most importantly, complex **1** did not not show any hydrogenation activity in the absence of a strong base. Table S1 in the Supporting Information contains additional information on the hydrogenation of the benchmark substrate in common basic N-donor solvents (pyridine, triethylamine, and tetramethylethylenediamine), where in none of the reaction media was proper catalytic activity observed.

To improve upon the results obtained in diglyme, we first aimed to reduce the rather high amount of the auxiliary base (20 mol % with respect to the substrate). Indeed, the reaction also proceeds with full conversion of the substrate when an equimolar amount of base versus complex **1** is present in the reaction mixture (Table 3, entries 1 and 2). However, owing to reproducibility problems in reactions that employed an equimolar amount of *t*-BuOK versus **1**, all subsequent base-optimized reactions were performed with 6 mol % of the given alcoholate and 5 mol % catalyst loading. Next, we lowered the amount of compound **1**, but to our dismay we observed a steep decrease in the catalytic performance (entries 3−6). We then continued our study by variation of reaction time, temperature, and H_2 pressure. Very interestingly, the catalyst enables full conversion after a reaction period of only 4 h (entry 7) and, encouraged by this finding, we also reduced the reaction temperature and hydrogen pressure. However, when these parameters were reduced, the activity of the given catalyst dropped significantly (entries 8 and 9).

In order to verify the homogeneous nature of complex **1** in combination with *t*-BuOK, we performed a mercury-poisoning experiment. For this purpose, the pertinent catalytic transformation was conducted in the presence of a few drops of elemental mercury. When the optimized reaction conditions for this experiment were applied, we did not observe any loss of catalyst activity. Hence, we have to infer that the given catalyst system operates through a homogeneous pathway.

With the optimized reaction conditions in hand, coordination compound **1** was then compared with the congeneric

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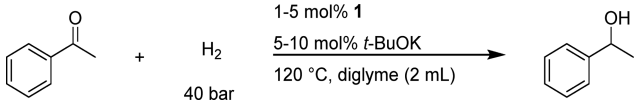
Table 3. Optimization of the Reaction Conditions for the Reduction of Acetophenone Catalyzed by 1[a]

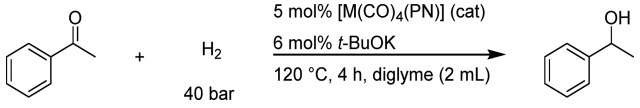


entry	catalyst loading (mol %)	*t*-BuOK (mol %)	*t* (h)	conversion (%)	yield (%)
1	5	10	18	>99	99
2	5	5	18	>99	99
3	2.5	10	18	30	27
4	2.5	5	18	15	14
5	1	10	18	25	23
6	1	5	18	8	7
7	5	6	4	>99	99
8[b]	5	6	6	82	82
9[c]	5	6	4	24	23
10	0	6	4	0	0
11	5	6	2	32	31

[a]A 0.5 mmol amount of acetophenone was used. Conversions and yields were determined by GC-MS analysis using *n*-dodecane as the internal standard. [b]The applied hydrogen pressure was 20 bar. [c]The reaction temperature was 100 °C.

group 6 metal complexes **2** and **3**. Regrettably, these complexes showed either very low or even no catalytic activity in the reduction of acetophenone, which underpins the special role of chromium as metal center for this particular catalytic reaction (Table 4). Tables S2 and S3 in the Supporting Information

Table 4. Catalytic Hydrogenation of Acetophenone Using the Group 6 Metal Carbonyl Complexes with the Optimized Reaction Conditions[a]



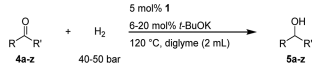
group 6 metal M in $[M(CO)_4(PN)]$	conversion (%)	yield (%)
Cr	>99	99
Mo	4	4
W	0	0

[a]A 0.5 mmol amount of acetophenone was used. Conversions and yields were determined by GC-MS analysis using *n*-dodecane as the internal standard.

summarize additional results for the acetophenone hydrogenation that were obtained with complexes $[Mo(CO)_4PN]$ and $[W(CO)_4PN]$ in combination with different solvents and bases.

In order to establish the scope and limitations of the catalytic system described herein, we applied a broad array of structurally diverse ketones (Table 5). We soon realized that the optimized reaction conditions for the acetophenone reduction were applicable to only a limited number of substrates, i.e. benzophenone **4a**, the benzoannelated congeners **4b**,**c**, propiophenone **4d**, and acetophenones equipped with methyl groups at the aromatic ring **4f**−**h**. However, it seems that increased steric bulk in close vicinity of the carbonyl group is well accommodated by the Cr-based catalyst, provided the substituent has an electron-releasing nature (entries 1, 4, and 6). When the cycloaliphatic derivative **4e** was used as the substrate for the hydrogenation, we had to significantly

Table 5. Scope and Limitations for the Hydrogenation Reaction of Ketones Catalyzed by 1[a]



Entry	Substrate		Target Product		Reaction Conditions[b]	Conversion (%)[c]	Yield (%)[d]
1		4a		5a	A	>99	99 (88)
2		4b		5b	B	>99	99 (90)
3		4c		5c	A	>99	98 (91)
4		4d		5d	A	>99	99 (40)
5		4e		5e	C	>99	99
6		4f		5f	A	>99	99
7		4g		5g	A	>99	98
8		4h		5h	A	>99	99 (64)
9		4i		5i	C	12	3
10		4j		5j	C	>99	70
11		4k		5k	C	45	20
12		4l		5l	C	36	6[e]
13		4m		5m	C	96	56
14		4n		5n	C	62	32[e]
15		4o		5o	C	27	4[e]
16		4p		5p	C	50	8[e]
17		4q		5q	C	36	2[e]
18		4r		5r	C	55	0[e]
19		4s		5s	C	>99	99
20		4t		5t	C	55	48
21		4u		5u	D	>99	99 (97)
22		4v		5v	C	25	0
23		4w		5w	C	>99	42
24		4x		5x	C	65	0
25		4y		5y	A	78	3
26		4z		5z	C	48	0

[a]A 0.5 mmol amount of the ketone was used. [b]Conditions **A**: *t*-BuOK (6 mol %), 40 bar of H_2, 4 h. Conditions **B**: *t*-BuOK (6 mol %), 50 bar of H_2, 12 h. Conditions **C**: *t*-BuOK (20 mol %), 50 bar of H_2, 20 h; Conditions **D**: *t*-BuOK (7.5 mol %), 50 bar of H_2, 14 h. [c]Conversions were determined by GC-MS analysis using *n*-dodecane as the internal standard. For **5f**,**g** *n*-hexadecane was used as the

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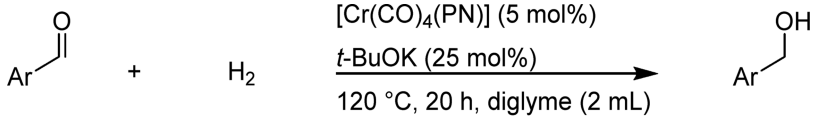
Table 5. continued

internal standard. [d]Yields were determined by GC-MS using *n*-dodecane as internal standard; isolated yields are givenin parentheses. [e]Hydrodehalogenation was observed.

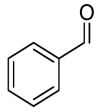
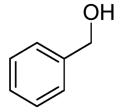
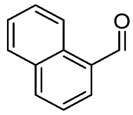
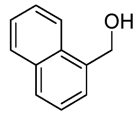
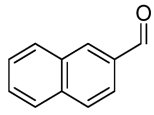
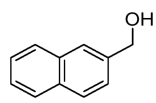
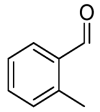
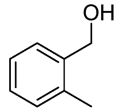
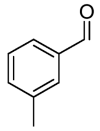
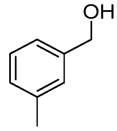
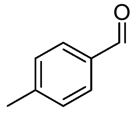
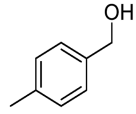
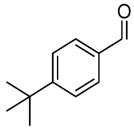
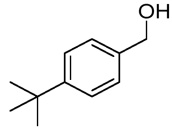
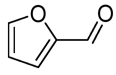
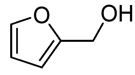
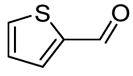
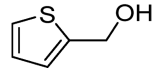
increase the reaction time (20 h), base loading (20 mol %), and H_2 pressure (50 bar) in order to maintain both complete conversion and high yield (entry 5). Electron-donating methyl groups at either position of the phenyl ring did not affect the catalyst performance (entries 6−8), and accordingly we obtained full conversions with excellent yields under the optimized reaction conditions. Consequently, the effect of electron-withdrawing groups located on the aromatic ring (fluoro-, chloro-, and bromoacetophenones) was then established on using the respective halide derivatives. The pertinent substituent in the *ortho* position gave rise to very low conversions and yields, whereas substrates **4l,o** were also prone to hydrodehalogenation under the reaction conditions (entries 9, 12, and 15). Notably, decent catalytic activity and medium yields were only observed if the halide group was placed in the *meta* position, but this assertion does not apply to the bromo derivative **4p** (entries 10, 13, and 16). The notoriously reactive compound **4r** did not produce any desired alcohol; instead, we only detected the untagged acetophenone in the GC-MS spectrum as the result of hydrodebromination. To our delight, substrate **4s** bearing an electron-withdrawing CF_3 group in the *meta* position was neatly converted to **5s**, albeit with harsher reaction conditions in comparison to those for the parent propiophenone (entry 19). Interestingly, the regioisomer **4t** with a shifted keto group produced the alcohol **5t** in only 48% yield under the same conditions (entry 20).

We then tested N-heterocyclic ketones (**4v−x**) as substrates; in these experiments the desired alcohol was only observed when the nitrogen atom was fixed in the *meta* position (Table 5, entries 22−24). When carbocyclic indanone (**4y**) was

Table 6. Hydrogenation of Aldehydes Catalyzed by Cr-Based Catalyst 1[a]



6a-i 50 bar **7a-i**

Entry	Substrate		Target Product		Conversion (%)	Yield (%)
1		**6a**		**7a**	97	74
2		**6b**		**7b**	94	79
3		**6c**		**7c**	81	45
4		**6d**		**7d**	>99	63
5		**6e**		**7e**	>99	79
6		**6f**		**7f**	>99	70
7		**6g**		**7g**	94	66
8		**6h**		**7h**	61	26
9		**6i**		**7i**	54	23

[a]A 0.5 mmol amount of the aldehyde was used. Conversions and yields were determined by GC analysis using *n*-dodecane as the internal standard.

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subjected to the hydrogenation procedure, we obtained a deep blue solution on completion of the reaction but the secondary alcohol **5y** was only formed in a trace amount (3%, entry 25). The fact that 4-acetylbenzonitrile (**4z**) does not give rise to any product **5z** proves that the given catalyst system is not compatible with CN groups.

In cases where we did not observe any alcohol formation but significant substrate conversion, we invoke the generation of high-molecular-weight products which were poorly volatile such that they could not be detected by the GC-MS device. Given the high base loading and a temperature of 120 °C, competing and predominant polycondensation reactions might occur that eventually produce such products which were sometimes deeply colored (cf. the hydrogenation of **4y**).

Finally, we extended the substrate scope to aldehydes (Table 6), where significantly harsher reaction conditions with respect to the base loading had to be applied because the reaction under the acetophenone-optimized conditions led to only a low conversion of benzaldehyde (**6a**). As already mentioned for acetophenone derivatives, the catalyst readily copes with steric hindrance and the corresponding alcohol was obtained in medium yields ranging from 63 to 79% (entries 1 and 4−7). Furthermore, it is worth noting that Cr catalyst **1** exhibits only mediocre catalytic activity against heterocyclic aldehydes such as furfural (**6h**) and thiophene-2-carboxaldehyde (**6i**). Due to the high *t*-BuOK loading, base-induced polycondensation and/or ring-opening reactions are likely to take place that significantly contribute to the substrate conversion. These processes give rise to low-volatility products and clearly exacerbate the selective formation of the primary alcohols from the respective aldehydes.

CONCLUSION

Our study toward the development of $[Mn(CO)_3(PN)Br]$-emulated catalysts based on group 6 metals resulted in the preparation of a series of the three halide-free organometallic complexes $[M(CO)_4(PN)]$, where M = Cr, Mo, W. The coordination compounds were synthesized in a straightforward manner from the respective metal carbonyl and commercially available 2-(diphenylphosphino)ethylamine, whereas the complexes were then characterized through X-ray crystallography, HR-MS, and IR and NMR spectroscopy. A decent catalytic activity in the homogeneous hydrogenation of acetophenone to afford the corresponding secondary alcohol was demonstrated with the compound $[Cr(CO)_4(PN)]$ in diglyme, provided that an excess of *t*-BuOK versus the catalyst was present in the reaction mixture. The molybdenum congener displayed only minor activity in the pertinent catalytic transformation, whereas the corresponding tungsten compound was not catalytically active at all. The privileged $[Cr(CO)_4(PN)]$ complex was thereafter applied to the related hydrogenation of aromatic aldehydes to yield the corresponding primary alcohols, whereas the catalytic performance of the given catalyst was significantly weaker in comparison to the acetophenone reduction. The optimized catalytic protocol described herein is free from the requirement for adding high loadings of a sensitive auxiliary hydride reagent that usually plagues related catalytically active systems. Given the fact that reports on homogeneous chromium-based hydrogenation catalysts are still scarce, we think that our contribution might open new vistas for the development of efficient catalytic protocols facilitated by this abundant non-noble metal.

EXPERIMENTAL SECTION

General Information. All chemicals were purchased from Merck (including Sigma-Aldrich), Acros Organics, Alfa Aesar, VWR, Roth, TCI, Lancaster Synthesis, or Chem Lab and were used as received without further purification. Hydrogenation reactions were carried out in a 300 mL autoclave from Parr Instruments GmbH, and the hydrogen employed with a purity of 5.0 was purchased from Linde Gas GmbH. Dry solvents were received from a MB-SPS-7 solvent system from M. Braun GmbH or purchased from Acros Organics. GC-MS analysis was carried out on a Shimadzu GC-MS QP-2020 instrument with helium (5.0 purity from Linde Gas GmbH) as the carrier gas. Infrared spectroscopy was performed in the solid state on a Bruker Tensor 27 ATR, and high-resolution mass spectra were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL. NMR measurements were performed on a Bruker Avance 300 and 500 MHz spectrometer. Spectra for different cores were recorded as follows: 300 MHz for ^{1}H NMR, 75.5 or 125.8 MHz for ^{13}C NMR, and 121.54 MHz for ^{31}P NMR. Chemical shifts are listed in parts per million (ppm) on the delta scale (δ). Axis calibration of the ^{1}H and ^{13}C NMR spectra is based on the nondeuterated solvent as reference. For the irradiation procedure in the respective product isolation steps an EvoluChem LED spotlight device (450 nm, 30 W) was used.

Safety Statement Concerning High-Pressure Hydrogenation. The pressurized H_2 container (200 bar, 50 L) was placed in a safety storage cabinet with an integrated tapping point. The pressure cylinder was connected to a control panel for the fine adjustment of the H_2 pressure used for the hydrogenation reactions. The loading of the autoclaves was performed in a fume hood that was equipped with a hydrogen sensor which was wired to a magnetic valve that instantaneously stopped the gas supply in case of any H_2 leakage that might occur during the filling procedure. Furthermore, both optical and acoustic alarm signals were triggered whenever free H_2 was detected inside the hood.

General Procedure for the Synthesis of Precursor Salts $[M(CO)_5Br][NEt_4]$ (M = Cr, Mo, W). These complexes were prepared according to a modified literature method.[9] The respective group 6 metal carbonyl $[M(CO)_6]$ (0.68 mmol, 1.5 equiv), where M = Cr, Mo, W, and tetraethylammonium bromide, NEt_4Br (95 mg, 0.45 mmol, 1.0 equiv), were placed in a flame-dried Radleys reaction tube, and the reactants were then suspended in dry glyme (8 mL). Thereafter, the reaction mixture was heated to a certain temperature (Cr, 120 °C; Mo, 80 °C; W, 130 °C), which was kept for a given period of time (Cr, 90 min; Mo, 150 min; W, 80 min). The reaction solution was then filtered off while still hot in order to remove residual solids, and the clear filtrate was warmed to room temperature. Precipitation of the title compounds was initiated upon slow addition of *n*-pentane (20 mL), and the resulting suspension was then cooled to −40 °C for 2 h. The crystals that formed were filtered off, washed with three small portions of diethyl ether, and finally dried *in vacuo*.

Tetraethylammonium Bromopentacarbonylchromate(0), $[Cr(CO)_5Br][NEt_4]$. In the synthesis, 150 mg of $[Cr(CO)_6]$ was used and the reaction mixture was refluxed at 120 °C for a period of 90 min. This afforded 152 mg (0.38 mmol, 84% yield) of the title compound, which was isolated as an orange crystalline powder. IR (ATR, cm^{-1}): 2060 ($\tilde{\nu}_{CO}$), 1898 ($\tilde{\nu}_{CO}$), 1865 ($\tilde{\nu}_{CO}$). The measured values are well in accord with the literature data.[9]

Tetraethylammonium Bromopentacarbonylmolybdate(0), $[Mo(CO)_5Br][NEt_4]$. The synthesis relied on the use of 180 mg of $[Mo(CO)_6]$, and the reaction mixture was heated to 80 °C for a period of 150 min. This afforded 159 mg (0.36 mmol, 80% yield) of the title compound, which was isolated as a yellow crystalline powder. IR (ATR, cm^{-1}): 2068 ($\tilde{\nu}_{CO}$), 1899 ($\tilde{\nu}_{CO}$), 1861 ($\tilde{\nu}_{CO}$). The measured values are well in accord with the literature data.[9]

Tetraethylammonium Bromopentacarbonyltungstate(0), $[W(CO)_5Br][NEt_4]$. For the preparation of the title compound 239 mg of $[W(CO)_6]$ was applied and the reaction mixture was refluxed at 130 °C for a period of 80 min. This afforded 205 mg (0.38 mmol, 85% yield) of the ionic carbonyl complex, which was isolated as a yellow crystalline powder. IR (ATR, cm^{-1}): 2066 ($\tilde{\nu}_{CO}$), 1897 ($\tilde{\nu}_{CO}$),

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1857 ($\tilde{\nu}_{CO}$). The measured values are well in accord with the literature data.[9]

Synthesis of Tetracarbonyl(2-(diphenylphosphino)-ethylamine)chromium(0), [Cr(CO)$_4$(PN)] (1). *Method A.* The solids [Cr(CO)$_6$] (100 mg, 0.45 mmol, 1.5 equiv) and NEt$_4$Br (64 mg, 0.31 mmol, 1.0 equiv) were placed in a flame-dried Radleys glass tube and then suspended in dry glyme (10 mL). Afterward, the reaction mixture was heated to 120 °C and kept at reflux for a period of 80 min, whereupon the solids were filtered off while the suspension was still hot. The clear filtrate was transferred into an argon-flushed Schlenk flask (25 mL), and thereafter a solution of 2-(diphenylphosphino)ethylamine (86 mg, 0.38 mmol, 1.2 equiv) in dry glyme (1 mL) was added. The mixture was agitated at 50 °C for 40 min and then refluxed at 120 °C for a further period of 2 h. After that, the suspension was cooled to room temperature, whereupon the recovered NEt$_4$Br was removed by filtration. To the resulting yellow solution was then added *n*-pentane (25 mL) in order to initiate product precipitation. Storage in the refrigerator (−40 °C) overnight and subsequent filtration afforded 44 mg (0.11 mmol, 36% yield) of the title compound as a yellow microcrystalline powder.

Method B.[16] A dry pressure tube was initially charged with 2-(diphenylphosphino)ethylamine (229 mg, 1.00 mmol, 1.0 equiv). Under an argon atmosphere, the ligand was dissolved in 10 mL of dry *n*-octane and [Cr(CO)$_6$] (220 mg, 1.00 mmol, 1.0 equiv) was added to the ligand solution. The resulting mixture was stirred at 140 °C overnight. The precipitate that formed was filtered off, washed with 10 mL of *n*-pentane, and finally dried with a vacuum pump. This afforded 338 mg (0.86 mmol, 86% yield) of the title compound as a yellow crystalline powder. Crystals suitable for X-ray analysis were obtained via slow diffusion of *n*-pentane into a solution of [Cr(CO)$_4$(PN)] in THF. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.71−7.64 (m, 4H), 7.45−7.42 (m, 6H), 2.92−2.77 (m, 2H), 2.39−2.32 (m, 4H) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 63.3 ppm. ^{13}C{^{1}H} NMR (125.8 MHz, $(CD_3)_2CO$, 20 °C): δ 229.1, 229.0, 228.0 (d, J = 2.6 Hz), 220.2 (d, J = 14.2 Hz), 138.2 (d, J = 33.4 Hz), 132.5 (d, J = 11.3 Hz), 130.6 (d, J = 2.0 Hz), 129.5 (d, J = 9.1 Hz), 44.6 (d, J = 12.8 Hz), 28.9 (d, J = 18.4 Hz) ppm; IR (ATR, cm^{-1}): 3336 ($\tilde{\nu}_{NH_2}$), 3288 ($\tilde{\nu}_{NH_2}$), 2005 ($\tilde{\nu}_{CO}$), 1906 ($\tilde{\nu}_{CO}$), 1866 ($\tilde{\nu}_{CO}$), 1818 ($\tilde{\nu}_{CO}$). HR-MS (ESI+) m/z: calcd for $C_{18}H_{16}CrNO_4P$, 393.0217 [M]$^+$; found, 393.0218.

Synthesis of Tetracarbonyl(2-(diphenylphosphino)-ethylamine)molybdenum(0), [Mo(CO)$_4$(PN)] (2). *Method A.* In a flame-dried Schlenk flask (25 mL) were placed [Mo(CO)$_6$] (75 mg, 0.28 mmol, 1.0 equiv) and 2-(diphenylphosphino)ethylammonium tetrafluoroborate (90 mg, 0.28 mmol, 1.0 equiv), which were then suspended in *n*-heptane (8 mL). Triethylamine was then added (50 μL, 0.36 mmol, 1.3 equiv), and thereafter the reaction mixture was heated to 130 °C and kept at this temperature for a period of 19 h with stirring. The crude product was filtered off and recrystallized from a hot acetone/water mixture (1/1 by volume). This afforded 78 mg (0.18 mmol, 64% yield) of the title compound which was obtained as a yellow crystalline powder.

Method B.[16] A dry pressure tube was charged with a magnetic stirring bar and 2-(diphenylphosphino)ethylamine (115 mg, 0.50 mmol, 1.0 equiv). Under an argon atmosphere, the ligand was dissolved in 10 mL of dry *n*-heptane and [Mo(CO)$_6$] (132 mg, 0.50 mmol, 1.0 equiv) was added to the solution. The resulting mixture was heated to 130 °C and stirred overnight. The precipitate was filtered off, washed with 10 mL of *n*-pentane, and finally dried *in vacuo*. This afforded 180 mg (0.41 mmol, 82% yield) of the title compound as a yellow crystalline powder. Crystals of X-ray quality were obtained via slow diffusion of *n*-pentane into a solution of [Mo(CO)$_4$(PN)] in toluene. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.71−7.64 (m, 4H), 7.45−7.42 (m, 6H), 3.05−2.90 (m, 2H), 2.65 (s, 2H), 2.36 (q, J = 6.4 Hz, 2H) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 42.7 ppm. ^{13}C{^{1}H} NMR (125.8 MHz, $(CD_3)_2SO$, 20 °C): δ 220.7, (d, J = 7.6 Hz), 218.4, 218.2, 209.1 (d, J = 9.4 Hz), 136.2 (d, J = 32.7 Hz), 131.6 (d, J = 13.0 Hz), 129.9, 128.7 (d, J = 9.3 Hz), 43.6 (d, J = 12.0 Hz), 27.6 (d, J = 20.4 Hz) ppm. IR (ATR, cm^{-1}): 3335 ($\tilde{\nu}_{NH_2}$), 3284 ($\tilde{\nu}_{NH_2}$), 2015 ($\tilde{\nu}_{CO}$), 1913 ($\tilde{\nu}_{CO}$), 1872 ($\tilde{\nu}_{CO}$), 1822 ($\tilde{\nu}_{CO}$); HR-MS (ESI+) m/z: calcd for $C_{17}H_{17}MoNO_3P$, 411.9995 [M + H − CO]$^+$; found, 411.9986.

Synthesis of Tetracarbonyl(2-(diphenylphosphino)-ethylamine)tungsten(0), [W(CO)$_4$(PN)] (3). *Method A.* In a flame-dried 20 mL Radleys glass tube were placed [W(CO)$_6$] (160 mg, 0.45 mmol, 1.5 equiv) and NEt$_4$Br (63 mg, 0.30 mmol, 1.0 equiv), whereupon the solids were suspended in dry glyme (8 mL). Under an argon atmosphere, the mixture was then stirred at 130 °C for a period of 90 min, whereupon the suspension turned yellow upon heating and agitation. Then the reaction mixture was filtered while still hot and the clear filtrate was directly transferred into a flame-dried Schlenk flask (25 mL). After that, 2-(diphenylphosphino)ethylamine (75 mg, 0.33 mmol, 1.1 equiv) was added and the mixture was heated to 120 °C and kept at reflux for 5 h. The reaction solution was then cooled to room temperature, upon which *n*-pentane (20 mL) was slowly added in order to initiate product precipitation. The resulting suspension was stored in the refrigerator (4 °C) overnight, and the crude product was thereafter recrystallized from a hot acetone/water mixture (1/1 by volume). This afforded 61 mg (0.12 mmol, 39% yield) of the title compound as yellow needles, which were collected on filter paper and eventually dried with a vacuum pump.

Method B.[16] Under an argon atmosphere, 2-(diphenylphosphino)-ethylamine (115 mg, 0.50 mmol, 1.0 equiv) was dissolved in 10 mL of dry mesitylene in a pressure tube. To this solution was added [W(CO)$_6$] (176 mg, 0.50 mmol, 1.0 equiv), and the resulting mixture was stirred at 190 °C overnight. Afterward, the precipitate was filtered off, washed with 10 mL of *n*-pentane, and subsequently dried with a vacuum pump. This afforded 200 mg (0.38 mmol, 76% yield) of the title compound as a yellow crystalline powder. Crystals suitable for X-ray crystallography were obtained through slow diffusion of *n*-pentane into a solution of [W(CO)$_4$(PN)] in toluene. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.71−7.64 (m, 4H), 7.45−7.43 (m, 6H), 3.17−3.07 (m, 2H), 3.03 (s, 2H), 2.38 (q, J = 6.4 Hz, 2H) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ 35.9 ppm. ^{13}C{^{1}H} NMR (125.8 MHz, $(CD_3)_2SO$, 20 °C): δ 211.4, 211.2, 211.2, 203.8 (d, J = 7.4 Hz), 135.9 (d, J = 38.8 Hz), 131.7 (d, J = 12.3 Hz), 130.1 (d, J = 1.6 Hz), 128.7 (d, J = 9.6 Hz), 45.6 (d, J = 11.4 Hz), 28.3 (d, J = 24.0 Hz) ppm. IR (ATR, cm^{-1}): 3326 ($\tilde{\nu}_{NH_2}$), 3278 ($\tilde{\nu}_{NH_2}$), 2010 ($\tilde{\nu}_{CO}$), 1905 ($\tilde{\nu}_{CO}$), 1862 ($\tilde{\nu}_{CO}$), 1815 ($\tilde{\nu}_{CO}$). HR-MS(ESI+) m/z: calcd for $C_{18}H_{17}WNO_4P$, 526.0399 [M + H]$^+$; found, 526.0399.

Hydrogenation Reactions Conducted with Complexes Incorporating Group 6 Metals (1−3). A 4 mL glass vial was initially charged with a magnetic stirring bar, **1** (0.025 mmol), the substrate (0.5 mmol), and *n*-dodecane (12 mg) as internal standard. After that, 2 mL of diglyme was added and the resulting yellow solution was treated with *t*-BuOK (0.03−0.125 mmol). The reaction vessel was then sealed with a septum cap that was equipped with a syringe needle. The glass vial was placed in a drilled Al plate and transferred into the 300 mL autoclave. After that, the autoclave was tightly sealed, purged three times with 30 bar of H_2, and finally pressurized to the required value. The autoclave was placed on a preheated stirring plate and heated to 120 °C. On completion of the catalytic transformation, the autoclave was cooled in a water bath. Afterward, the H_2 pressure was slowly released and the solutions were degassed upon stirring in air for 5 min. Finally, a 30 μL aliquot was taken from each vial, mixed with 1 mL of acetone, and eventually analyzed by GC-MS. For hydrogenation experiments that involved product isolation in the final step, the reaction vials were charged without *n*-dodecane.

General Procedure for the Isolation of the Hydrogenation Products. For the product isolation we fruitfully exploited the photoinstability of complex **1** at 450−490 nm (blue region). First, the yellow reaction solution was irradiated (450 nm, 30 W) until complete decoloration and then the resulting suspension was diluted with 1 mL of dichloromethane (DCM). The mixture was filtered through a plug of silica (2 cm in a Pasteur pipet) that was then washed with 2 mL of DCM. Finally, the clear filtrate was evaporated to dryness, leaving behind the corresponding alcohol.

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*Diphenylmethanol (**5a**).* The title compound was synthesized according to the standard procedure described above using 90.9 mg (0.499 mmol) of benzophenone **4a**: colorless crystals, 81.3 mg (0.441 mmol, 88% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.40−7.24 (m, 10H), 5.83 (s, 1H), 2.41 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 20 °C): δ 144.6, 128.8, 127.8, 126.8, 76.4 ppm.

*1-Naphthylethanol (**5b**).* The compound was prepared according to the standard procedure described above using 85.1 mg (0.500 mmol) of 1-acetonaphthone **4b**: colorless oil, 77.8 mg (0.452 mmol, 90% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 8.13−8.10 (m, 1H), 7.92−7.88 (m, 1H), 7.81−7.78 (m, 1H), 7.69−7.66 (m, 1H) 7.55−7.46 (m, 3H), 5.63 (q, J = 6.5 Hz, 1H), 2,40 (s, 1H), 1.63 (d, J = 6.5 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 20 °C): δ 142.1, 134.2, 130.7, 129.2, 128.1, 126.3, 125.9, 125.9, 123.7, 122.4, 67.2, 24.7 ppm.

*2-Naphthylethanol (**5c**).* The compound was synthesized according to the standard procedure using 85.0 mg (0.499 mmol) of 2-acetonaphthone **4c**: white crystalline powder, 78.1 mg (0.453 mmol, 91% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.90−7.86 (m, 4H), 7.56−7.48 (m, 3H), 5.09 (q, J = 6.4 Hz, 1H) 2.10 (s, 1H), (d, J = 6.5 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 20 °C): δ 144.0, 133.8, 133.3, 128.5, 128.2, 128.0, 126.5, 126.1, 124.3, 124.1, 70.7, 25.5 ppm.

*1-Phenylpropan-1-ol (**5d**).* The title compound was synthesized according to the standard procedure using 67.1 mg (0.500 mmol) of propiophenone **4d**: colorless oil, 27.4 mg (0.201 mmol, 40% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.35−7.26 (m, 5H), 4.58 (t, J = 6.5 Hz, 1H), 1.93 (s, 1H), 1.83−1.67 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 20 °C): δ 145.4, 128.7, 127.7, 126.3, 76.1, 32.5, 10.3 ppm.

*1-(3-Methylphenyl)ethanol (**5h**).* The alcohol was prepared following the standard procedure using 67.1 mg (0.500 mmol) of 3-methylacetophenone **4h**: colorless oil, 43.3 mg (0.318 mmol, 64% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.25−7.07 (m, 5H), 4.84 (q, J = 6.4 Hz, 1H), 2.35 (s, 3H) 1.92 (s, 1H), 1.45 (d, J = 6.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 20 °C): δ 146.5, 138.5, 128.6, 128.4, 126.4, 122.7, 70.6, 25.5, 21.6.

*1-(Ferrocenyl)ethanol (**5u**).* The title compound was synthesized according to the standard procedure, but the product isolation was performed in a slightly different manner. The orange reaction mixture was irradiated until it turned into a brownish suspension, which was then diluted with 1 mL of diethyl ether and filtered through a small pad of Celite (2 cm in a Pasteur pipet). The loaded Celite was washed with 2 mL of diethyl ether, and the filtrate was thereafter evaporated to dryness, leaving behind the desired alcohol. For the synthesis, 114.1 mg (0.500 mmol) of **4u** was applied: orange needles, 111.3 mg (0.484 mmol, 97% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 4.53 (q, J = 6.4 Hz, 1H), 4.22−4.16 (m, 9H), 1.92 (s, 1H) 1.44 (d, J = 6.4 Hz 3H) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 20 °C): δ 94.9, 68.4, 68.1, 68.0, 66.3, 66.2, 65.7, 23.8. HRMS (ESI+) m/z: calcd for $C_{12}H_{14}FeO$ $[M]^+$, 230.0394; found, 230.0392.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00612.

Additional hydrogenation experiments in coordinating solvents conducted with complexes **1**−**3** in the presence of different bases, ATR-IR, ^{1}H, ^{31}P, and $^{13}C\{^1H\}$ NMR, and HR-MS spectra of the carbonyl complexes $[M(CO)_4(PN)]$ (M = Cr, Mo, W), crystallographic data and ORTEP representations of compounds $[M(CO)_4(PN)]$ (M = Cr, Mo, W), ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the synthesized and isolated alcohols, and HR-MS spectra of the ferrocenyl alcohol **5u** (PDF)

Accession Codes

CCDC 2011626−2011628 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Christoph Topf − *Institute of Catalysis (INCA), Johannes Kepler University (JKU), 4040 Linz, Austria;* orcid.org/0000-0001-7595-3074; Email: christoph.topf@jku.at

Authors

Thomas Vielhaber − *Institute of Catalysis (INCA), Johannes Kepler University (JKU), 4040 Linz, Austria*

Kirill Faust − *Institute of Catalysis (INCA), Johannes Kepler University (JKU), 4040 Linz, Austria*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00612

Notes

The authors declare no competing financial interest.

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