Multiple Bonds Between Main-Group Elements and Transition Metals, CLXIV[◇]

Alkylrhenium(VI) Oxides – Synthesis and Characterization

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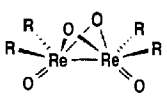
Received October 2, 1996

Keywords: Rhenium / Oxides / Alkyl ligands / Dirhenium compounds / Metal-metal interactions

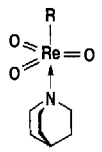
Most alkylrhenium(VII) oxides, e.g. ((*cyclo*)-C_3H_5)ReO_3 (**2**) are rather sensitive to temperature and moisture with the prominent exception of methyltrioxorhenium (**1**). The corresponding alkylrhenium(VI) oxides of formula [RR'(O)-Re(μ−O)]$_2$ [R = R' = (*cyclo*)-C_3H_5 (**3**), *i*Pr (**4**); R = CH_3, R' = C_2H_5 (**5**), R = CH_3, R' = *i*Pr (**6**)] are much more stable in this regard. They can be handled in air at room temperature. They were synthesized from Re_2O_7 and dialkylzinc precursors, fully characterized and are available in much higher yields than their Re^{VII} congeners. Mixed tetraalkyltetraoxodirhenium(VI) complexes (R ≠ R') synthesized from **1** and dialkylzinc compounds form as a mixture of *cis/trans* isomers. They are oily liquids at room temperature. The Re=O and Re−Re stretching force constants as a measure of the bond strengths, were determined from IR and Raman data.

Alkylrhenium(VI) oxides of formula [R_2(O)Re(μ-O)]$_2$ (**I**) are known for 10 years[2]. However, it was not until recently, that one of them, [$(CH_3)_2$(O)Re(μ-O)]$_2$, has been used as a catalyst in olefin epoxidation[3]. It has been shown that this compound forms the same catalytically active species in the presence of H_2O_2 as CH_3ReO_3 (**1**). The latter compound is one of the most efficient oxidation catalysts known to date[4]. Several other alkylrhenium(VII) oxides of general formula $RReO_3$ (**II**) also form catalytically active complexes with H_2O_2[3,5], particularly cyclopropyltrioxorhenium(VII) (**2**). The quinuclidine adduct of **2** [general formula $RReO_3 \cdot N(CH_2CH_2)_3CH$ (**III**)] is even more active and selective in olefin epoxidation than the quinuclidine adduct of **1**[3]. Unfortunately, all known alkylrhenium(VII) oxides are much less stable than **1**[6]. We were therefore tempted to synthesize some new tetraalkyltetraoxodirhenium(VI) derivatives to compare their stability with known alkyrhenium(VII) oxides in order to see whether they are possibly more stable and easier to handle than compounds of type **II**.



I (Re^{VI})

II (Re^{VII})



III (Re^{VII})

[◇] Part CLXIII: Ref.[1].

Results and Discussion

Reaction of dirhenium heptaoxide with dialkylzinc at low temperatures leads to the formation of bis[dialkyl(μ-oxo)oxorhenium(VI)] complexes of general formula [R_2(O)Re(μ-O)]$_2$ (equation 1). This way of preparation leads to cleaner products and higher yields than other methods described earlier[2]. We were especially interested in the synthesis of cyclopropyl and isopropyl derivatives because cyclopropyltrioxorhenium(VII) (**2**) is very unstable and only isolable as its quinuclidine adduct[6a] while several efforts failed to synthesize isopropyltrioxorhenium(VII)[6b]. Indeed, bis[dicyclopropyl(μ-oxo)oxorhenium(VI)] (**3**) is much more stable than **2**. It is a yellow powder decomposing at 140 °C and stable in air. It is soluble in THF, $CHCl_3$, CH_2Cl_2, CCl_4, and alkanes. Bis[diisopropyl(μ-oxo)oxorhenium(VI)] (**4**) can also be synthesized according to equation 1, but the yield is lower than in the case of **3**. A significant part of the Re^{VII} starting material is reduced to ReO_3 and ReO_2 even at −78 °C in the course of the reaction (IR evidence). This was confirmed by elemental analysis of the dark precipitates. Propane, hexanes and several organic oxidation products are also formed (GC/MS analysis). Obviously, the cyclopropyl complex is more readily formed than the isopropyl complex, both for compounds of type **I** and **II**. Compound **4** resembles **3** in its solubility but is less stable.

All compounds of type **I** described in this work are volatile and can be sublimed at room temperature in oil-pump vacuum. Therefore, they also can be easily examined by EI MS. In contrast to the Re^{VII} derivatives of type **II** and **III** which show only a very weak or no molecular peak, com-

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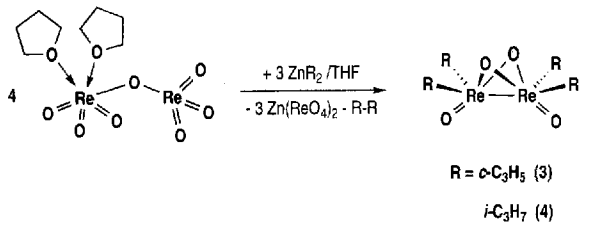
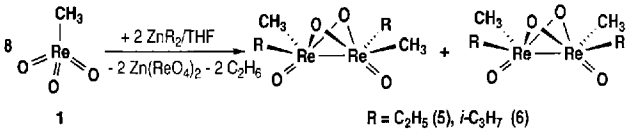


pounds **3**–**6** show pronounced molecular peaks. The most intensive peak of the EI-MS spectrum is the $[M/2]^+$ or $[M/2 - H_2]^+$ signal. The same is the case for the derivatives with R = CH_3 and R = C_2H_5[2c,d].

Reaction of **1** with dialkylzinc compounds at low temperatures in THF leads to the formation of mixed derivatives of formula $[(CH_3)R(O)Re(\mu\text{-}O)]_2$, R = C_2H_5 (**5**), $CH(CH_3)_2$ (**6**) (equation 2). During the reaction ethane and butane or propane and hexanes, respectively, are formed as well (GC/MS analyses). Compounds **5** and **6** are orange oils which solidify a few degrees below room temperature and are soluble in most common organic solvents. The surprisingly low melting point of these compounds stems from a *cis/trans* isomerism, as can be deduced from the spectroscopic data (see below). Derivative **5** decomposes at ca. 65 °C, **6** at ca. 30 °C.



An interesting reaction takes place when dicyclopropylzinc is treated with **1**. Instead of a mixed cyclopropyl methyl derivative according to equation 2 compound **3** is formed as the only organometallic oxide. This reaction takes place, regardless of the stoichiometry of the starting materials. Besides **3** only unreacted starting material and zinc perrhenate can be isolated. Furthermore, in the gas phase methane and ethane can be found. The latter is very likely formed by the coupling of two methyl radicals. The exact stoichiometry of this reaction is not yet clear. In the reactions described by equations 1 and 2, a certain amount of the Re^{VII} precursor is transformed to ReO_3 and ReO_2 (IR, NMR evidence, see above). Therefore, equations 1 and 2 have to be regarded as idealized and the isolated yields of **3**–**6** are strongly dependent on the extent of undesirable parallel reactions. The product yields of **3**–**6** are also strongly influenced by the reaction conditions. Slight variations of reaction temperature and concentration can lead to significantly lower yields and, in certain cases, to other products (see ref.[2d]).

Table 1 shows a comparison of selected ^{1}H-NMR data of alkylrhenium oxides. The signal of the α protons are shifted to higher field beginning from methyl to ethyl to cyclopropyl in case of type-**I** and type-**III** compounds. The signal of the α protons of type-**III** derivatives are generally shifted to higher field because of the strong electron-donor capability of the Lewis base quinuclidine. Unfortunately, no data for free **2** exist due to its instability. The α protons of the ethyl groups of derivative **5** are diastereotopic, leading to an AB-type pattern as it has been described for related compounds[2b,d]. In the case of compounds **5** and **6** two signal sets of different intensity are observed by ^{1}H NMR. The shift difference between the two signal sets is only a few Hz. A COSY ^{1}H-NMR spectrum reveals the same pattern. This phenomenon is very likely due to a *cis/trans* isomerism. This view is also supported by ^{17}O-NMR spectroscopy. While $(CH_3)_4Re_2O_4$ displays only two ^{17}O-NMR signals [$\delta(^{17}O)$ = 710 (terminal oxygen atoms) and 425 (bridging oxygen atoms)] the ^{17}O-NMR spectrum of **5** shows three different peaks [$\delta(^{17}O)$ = 705, 700 and 429]. All of the signals of **5** are broader than the signals of $(CH_3)_4Re_2O_4$, especially the signal which is due to the bridging atoms. This might be caused by an equilibrium process. It is known that the bridging oxygen atoms of type-**I** molecules can be easily exchanged[2]. Further investigation of compounds of type-**I** by means of ^{17}O-NMR spectroscopy is under way. As expected from the above-mentioned results it was not possible to separate the isomers by chromatography.

Table 1. ^{1}H-NMR shifts of the α protons of selected alkylrhenium oxides in C_6D_6 and $CHCl_3$ (δ values)

	R^1ReO_3•N(CH2CH2)3CH			$[R^1(R^2)O(\mu\text{-}O)Re]_2$			
R^1	CH_3	C_2H_5	*cyclo*-C_3H_5	CH_3	C_2H_5	*cyclo*-C_3H_5	CH_3
$\delta(^1H)$	1.40	1.48	2.30	2.81	2.89 4.13	3.71	2.80
R^2	–	–	–	CH_3	C_2H_5	*cyclo*-C_3H_5	C_2H_5
$\delta(^1H)$				2.81	2.89 4.13	3.71	3.14 4.22

Compounds **3**, **5** and $[(CH_3)_2ORe(\mu\text{-}O)]_2$ have also been closely examined by IR and Raman spectroscopy. The skeletal stretching modes are presented in Table 2 and assigned on the basis of normal coordinate calculation. Results of X-ray diffraction studies of $[(CH_3)_2ORe(\mu\text{-}O)]_2$ and $[(C_2H_5)_2ORe(\mu\text{-}O)]_2$[2c,d] are consistent with a model having C_{2v} symmetry with two Re–O–Re bridges and an Re–Re distance of approximately 260 pm. It was of special interest (having in mind possible applications of the described compounds) to clarify the appearance of the Re–Re and Re–O–Re stretching modes and to compare Re=O and Re–C stretching modes and force constants with the corresponding molecules of type **II**. Correspondence of IR and Raman bands of **5** indicate rather a C_s than a C_{2v} symmetry. Some characteristic stretching force constants are shown in Table 3. The stability of these compounds can be correlated with the Re–Re bond strength. The values of the Re=O stretching force constants are in general somewhat higher than the corresponding force constants in **1** and $C_2H_5ReO_3$ (8.309 and 8.252 Ncm^{-1}, respectively)[7]. The largest value of the Re–Re stretching force constant is found in the tetramethyl derivative, the smallest in the diethyldimethyl compound **5**.

Table 2. Skeletal stretching Raman bands of $R_4O_4Re_2$ molecules [cm^{-1}]

$ReCH_3$			$Re(CH_3)C_2H_5$		$Re(cyclo\text{-}C_3H_5)$		Assignment	
obsd.		calcd.	obsd.		obsd.			
1018	s[a]	1118	1021	s	998	s	a_1	Re=O str
1011	sh	1011	1010	sh			b_1	
866	vvw, p	868	871	w	864	w	a_1	Re–O str
818	vvw	834	806	w	836	m	b_2	
					819	m		
754	vw	770	752	m	780	vw	b_1	
728	vw	744	735	w	746	w, m	a_2	
552	m, p	551	537	s	528	vw	a_1	Re–C str
529	m	548	735	w			b_1	
509	w, sh	507	511	m			a_1	
500	w, p	506	496	m	480	vw	b_2	
189	vvs, p	186	177	vs	181	vs	a_1	Re–Re str

[a] vvs = extremely strong, vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = extremely weak, sh = shoulder.

Table 3. Selected stretching force constants for $R_4O_4Re_2$ molecules [10^2 Nm^{-1}]

	$R = CH_3$	$R = CH_3, C_2H_5$	$R = cyclo\text{-}C_3H_5$
K(Re=O)	8.87	8.90	8.51
K(Re–Re)	1.56	1.37	1.43

Conclusions

Starting from Re_2O_7 or CH_3ReO_3 several alkylrhenium(VI) oxides were synthesized whose Re^{VII} congeners are either not available or very unstable. Most of the described Re^{VI} compounds can be synthesized in good yields. They are stable enough to be candidates for closer investigations of their chemistry. Several Re^{VI} derivatives, most prominently the cyclopropyl derivative may prove to be oxidation catalysts if one considers the properties of $RReO_3$ · quinuclidine in the presence of H_2O_2. Experiments are under way in our laboratories to verify these expectations.

We thank the *Deutsche Forschungsgemeinschaft*, the *Stiftung Volkswagenwerk*, the *DAAD*, and the *Alexander-von-Humboldt-Stiftung* (award to J. M.) for financial support. We wish to acknowledge Dr. *E. Pöl* (Garching), Dr. *T. Johnson* and Ms. *C. Lehner* (Bruker, Karlsruhe) for their help in recording Raman and FT-Raman spectra.

Experimental Section

All reactions were performed in Schlenk flasks under dry argon or dry nitrogen; solvents were dried and distilled under nitrogen with the standard methods. – Infrared spectra were recorded with a Perkin-Elmer 1650 Series FTIR and Nicolet FT-5DX spectrometer. – Raman spectra were recorded with a triple Raman Spectrometer manufactured by Instruments S. A. – The ^1H-, ^{13}C-, and ^{17}O-NMR spectra were recorded at 399.78, 100.5, and 54.21 MHz, respectively, with an FT JEOL GX 400 instrument and an JEOL JNM GX 270 instrument. All NMR solvents were "freeze-pump-thaw"-degassed and stored over molecular sieves (4 Å; CH_3CN: 3 Å) before use. – Elemental analyses were performed in the Microanalytical Laboratory of our institute. – Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer. – Gas chromatography was performed with an HP 5890 A with integrator HP 339 A and detector HP 5970 of Hewlett-Packard. – CH_3ReO_3 and $[(CH_3)_2ORe(\mu\text{-}O)]_2$ were prepared according to literature methods[2c,d,8], the preparation of dicyclopropylzinc was carried out according to ref.[9], all other zinc precursors were purchased from Aldrich and used without further purification. Re_2O_7 was prepared according to ref.[10]. ^{17}O-marked compounds were prepared from ^{17}O-marked methyltrioxorhenium(VII) and ^{17}O-marked $Re_2O_7 \cdot (THF)_2$[11].

1) *Bis[dicycloproyl(μ-oxo)oxorhenium(VI)]* (**3**): 1.00 g (2.0 mmol) of dirhenium heptaoxide is dissolved in 30 ml of THF and cooled to −30 °C. 17 ml of a 0.1 M solution of dicyclopropylzinc (1.70 mmol) in *n*-pentane is added dropwise via syringe. The formerly colorless solution turns brown within seconds and is stirred for additional 30 min. Then the solvent is removed completely in oil-pump vacuum and the remaining residue extracted with 50 ml of *n*-pentane. The dark orange solution is cleaned by means of column chromatography with reversed silica gel as stationary phase and *n*-pentane as mobile phase at −5 °C. After removal of the solvent, **3** is isolated as yellow powder. Yield: 230 mg (77%), m.p. 140 °C (dec.). – IR (KBr; cm^{-1}): $\tilde{\nu}$ = 2998 st, 1000 sst, 865 m. – Raman: see Table 2. – ^1H NMR ($CDCl_3$, 20 °C): δ = 0.69 (m, 1H, CH_2), 1.13 (m, 1H, CH_2), 1.66 (m, 1H, CH_2), 2.27 (m, 1H, CH_2), 3.71 (m, 1H, ReCH). – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 12.25 (CH_2), 14.66 (CH_2), 40.30 (ReCH). – EI-MS (70 eV); *m/z* (%): 602 (5) [M^+], 301 (55) [$M/2^+$], 299 (100) [$(M/2 - H_2)^+$]. – $C_{12}H_{20}O_4Re_2$ (600.58): calcd. C 23.92, H 3.32, O 10.36; found C 24.20, H 3.49, O 10.50.

2) *Bis(diisopropyl(μ-oxo)oxorhenium(VI)]* (**4**): 0.49 g (1.0 mmol) of dirhenium heptaoxide is dissolved in 30 ml of THF and cooled to −78 °C. 6.25 ml of a 0.48 M solution of diisopropylzinc (1.70 mmol) in diisopropyl ether is added dropwise via syringe. The formerly colorless solution turns dark-brown immediately and is stirred for additional 90 min at −60 °C. Then the solvent is removed completely in oil-pump vacuum at −25 °C and the remaining residue extracted with 30 ml *n*-pentane. The orange solution is purified by means of column chromatography with reversed silica gel as stationary phase and *n*-pentane as mobile phase at −25 °C. After removal of the solvent **4** is isolated as yellow powder. Yield 96 mg (63%), m.p. ca. 50 °C (dec.). – IR (KBr; cm^{-1}): $\tilde{\nu}$ = 2963 st, 1414 w, 1019 st, 866 m, 703 w, 400 m. – ^1H NMR ($CDCl_3$, 20 °C): δ = 1.54 (m, 6H, CH_3), 3.57 (m, 1H, ReCH). – ^{13}C NMR ($CDCl_3$, 20 °C): δ = 18.60 (CH_3), 38.30 (ReCH). – EI MS (70 eV); *m/z* (%): 608 (4) [M^+], 304 (100) [$M/2^+$]. – $C_{12}H_{28}O_4Re_2$ (608.75): calcd. C 23.68, H 4.64, O 10.51; found C 23.91, H 4.72, O 10.36.

3) *Bis[(ethyl)methyl(μ-oxo)oxorhenium(VI)]* (**5**): 0.5 g (2.0 mmol) of methyltrioxorhenium(VII) is dissolved in 10 ml of THF and cooled to −50 °C. 6 ml of a 1.0 M solution of diethylzinc (1.70 mmol) in *n*-hexane is added dropwise via syringe. The formerly colorless solution changes color to orange and is stirred for additional 30 min. The solution is warmed to room temp., then cooled to −25 °C and mixed with 0.14 ml (8 mmol) of distilled water to destroy excess diethylzinc. A voluminous, grey precipitate is formed immediately. All solvents are removed in oil-pump vacuum and the remaining residue extracted with 50 ml of diethyl ether. The orange extract is concentrated to 5 ml in oil-pump vacuum and cleaned by column chromatography with reversed silica gel as stationary phase and *n*-pentane as mobile phase at room temp. After removal of the solvent, **5** is isolated as orange oil. Yield 206 mg (79%), m.p. 20 °C, dec. at 65 °C. – IR (KBr; cm^{-1}): $\tilde{\nu}$ = 2948 m, 2861 m, 1453 m, 1359 w, 1367 w, 1261 w, 1229 w, 1182 st, 1026 sst, 940 m, 760 m, 538 w, 507 m, 490 w. – Raman: see Table 2. – ^1H NMR ($CDCl_3$, 20 °C): δ = 2.12 (dt, 3H, CH_2CH_3), 2.80 (ds, 3H, CH_3), 3.14 (m,

1 H, ReCH), 4.22 (m, 1 H, ReCH). – UV/Vis (*n*-pentane; nm): λ = 224 sst, 298 st, 310 sh, 374 m, 522 m. – EI MS (70 eV); *m/z* (%): 542 (44) [M^+], 522 (55) [$(M - H_2)^+$], 299 (100) [$(M/2)^+$]. – $C_6H_{16}O_4Re_2$ (524.29): calcd. C 13.75, H 3.07, O 12.20; found C 13.81, H 3.05, O 12.37.

4) *Bis[(isopropyl)methyl(μ-oxo)oxorhenium(VI)]* (**6**): 0.25 g (1.0 mmol) of methyltrioxorhenium(VII) is dissolved in 15 ml of THF and cooled to −70°C. 6.25 ml of a 0.48 M solution of diisopropylzinc (3.0 mmol) in diisopropyl ether is added dropwise via syringe. The color of the solution turns brown and the solution is stirred for additional 30 min. Then it is slowly warmed to −5°C, then cooled to −25°C and mixed with 0.07 ml (4 mmol) of distilled water to destroy excess diethylzinc. A voluminous, grey precipitate is formed immediately. All solvents are removed in oil-pump vacuum and the remaining residue is extracted with 25 ml of diethyl ether. The orange extract is concentrated to 4 ml in oil-pump vacuum and cleaned by column chromatography with reversed silica gel as stationary phase and *n*-pentane as mobile phase at −30°C. After removal of the solvent, **5** is isolated as orange oil. Yield 68 mg (49%), m.p. 14°C, dec. at ca. 30°C, slow decomposition even at −25°C. – IR (KBr; cm^{-1}): $\tilde{\nu}$ = 2963 m, 1457 w, 1021 sst, 983 m, 941 m, 418 m. – ^1H NMR (CD_2Cl_2, −20°C): δ = 1.89 [dd, 6 H, $CH(CH_3)$], 3.48 (m, 1 H, ReCH). – EI MS (70 eV): *m/z* (%) = 552 (14) [M^+], 276 (49) [$M/2^+$], 274 (100) [$(M/2 - H_2)^+$]. – $C_8H_{20}O_4Re_2$ (552.64): calcd. C 17.39, H 3.84, O 11.58; found C 17.11, H 3.81, O 11.67.

[1] W. A. Herrmann, F. E. Kühn, M. Mattner, G. R. J. Artus, M. Geisberger, J. D. G. Correia, *J. Organomet. Chem.*, in press.
[2] [2a] J. M. Huggins, D. R. Randolph, L. Lebioda, *J. Organomet. Chem.* **1986**, *312*, C15–C17. – [2b] S. Cai, D. M. Hoffman, J. C. Huffmann, D. A. Wierda, H. G. Woo, *Inorg. Chem.* **1987**, *26*, 3693–3700. – [2c] W. A. Herrmann, J. G. Kuchler, W. Wagner, J. K. Felixberger, E. Herdweck, *Angew. Chem.* **1988**, *100*, 420–422; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 294–296. – [2d] W. A. Herrmann, C. C. Romão, P. Kiprof, J. Behm, M. R. Cook, M. Taillefer, *J. Organomet. Chem.* **1991**, *413*, 11–25. – [2e] S. Cai, D. M. Hoffman, D. A. Wierda, *Inorg. Chem.* **1991**, *30*, 827–831.
[3] W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. Scherer, *J. Mol. Catal.* **1994**, *86*, 243–266.
[4] Review: W. A. Herrmann, *J. Organomet. Chem.* **1995**, *500*, 149–173, and literature cited therein.
[5] W. A. Herrmann, J. D. G. Correia, F. E. Kühn, G. R. J. Artus, C. C. Romão, *Chem. Eur. J.* **1996**, *2*, 168–173.
[6] [6a] W. A. Herrmann, F. E. Kühn, C. C. Romão, H. Tran Huy, M. Wang, R. W. Fischer, P. Kiprof, W. Scherer, *Chem. Ber.* **1993**, 45–50. – [6b] W. A. Herrmann et al., unpublished results, **1988–1993**.
[7] [7a] W. A. Herrmann, P. Kiprof, K. Rybdal, J. Tremmel, R. Blom, R. Alberto, J. Behm, R. W. Albach, H. Bock, B. Solouki, J. Mink, D. D. Lichtenberger, N. E. Gruhn, *J. Am. Chem. Soc.* **1991**, *113*, 6527–6537. – [7b] J. Mink, G. Keresztury, A. Stirling, W. A. Herrmann, *Spectrochimica Acta* **1994**, *50A*, 2039–2057. – [7c] F. E. Kühn, Ph. D. Thesis, Technische Universität München, **1994**.
[8] W. A. Herrmann, F. E. Kühn, R. W. Fischer, W. R. Thiel, C. C. Romão, *Inorg. Chem.* **1992**, *31*, 4431–4432.
[9] [9a] X. H. Thiel, S. Wilcke, M. Ehrhardt, *J. Organomet. Chem.* **1968**, *14*, 13. – [9b] Houben-Weyl, *Methoden der Organischen Chemie*, 4th ed., vol. XIII/2a, **1973**, 594.
[10] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, 3rd ed., Stuttgart, **1978**.
[11] [11a] W. A. Herrmann, F. E. Kühn, P. W. Roesky, *J. Organomet. Chem.* **1995**, *485*, 243–251. – [11b] W. A. Herrmann, F. E. Kühn, M. U. Rauch, J. D. G. Correia, G. Artus, *Inorg. Chem.* **1995**, *34*, 2941–2920.

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