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Iron Cyclopentadienyl(triphenylphosphine)carbonylphenyl Telluride Adducts with Manganese, Tungsten, and Rhodium Complexes

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Abstract—The reactions of $CpFe(CO)(PPh_3)TePh$ (**I**) with $CpMn(CO)_2(THF)$, $W(CO)_5(THF)$, and $[Cp^*RhCl_2]_2$ gave heterometallic adducts $CpFe(CO)(PPh_3)(\mu\text{-}TePh)CpMn(CO)_2$ (**II**), $CpFe(CO)(PPh_3)(\mu\text{-}TePh)W(CO)_5$ (**III**), and $CpFe(CO)(PPh_3)(\mu\text{-}TePh)RhCl_2Cp^*$ (**IV**). The structures of **II**, **III**, and **IV** · $3CDCl_3$ (CIF files CCDC nos. 063654, 1063655, 1038123) were studied by X-ray diffraction. In all complexes, metal atoms are connected by only one tellurophenyl bridge. All $M \rightarrow$ Te bonds are substantially shortened with respect to the sum of the covalent radii owing to the additional $M \rightarrow$ Te dative interactions.

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INTRODUCTION

The enhanced attention to heterometallic chalcogenide complexes is based not only on the diversity of structures and types of bonds but also on the possibility of thermally induced removal of organic moieties in such molecules in order to obtain complex inorganic materials, often inaccessible by other methods [1]. In particular, previously, we studied the thermal decomposition of the cobalt-, tungsten-, and tellurium-containing organometallic complex $Cb^*Co(CO)_2TePhW(CO)_5$ ($Cb^* = C_4M_4$) to give CoWTe [2]:

$$Cb^*Co(CO)_2TePhW(CO)_5$$
$$\xrightarrow[-2CO]{128-160°C} Cb^*CoTePhW(CO)_5$$
$$\xrightarrow[-5CO]{160-196°C} Cb^*CoWTePh \xrightarrow[-Ph]{196-209°C} Cb^*CoWTe$$
$$\xrightarrow[-C_4M_4]{209-300°C} CoWTe$$

In addition, in molecules containing two or more metal centers, cooperative interaction is possible, which can enhance the selectivity and efficiency of catalysis and initiate reactions that would be impossible with only one metallic center [3, 4]. Recently, as metal complexes functioning as ligands with respect to another metal, we used $CpFe(CO)_2TePh$ in combination with rhenium carbonyl chloride [5], and phosphine-substituted complex $CpFe(CO)(PPh_3)TePh$ (**I**), which reacted with $[CpMn(CO)_2(NO)]PF_6$ to give binuclear heterometallic cation $[CpFe(CO)(PPh_3)(\mu\text{-}TePh)Mn(CO)(NO)Cp]^+$ [6]. This communication describes the synthesis and structure of neutral adducts of **I** with organometallic manganese, tungsten, and rhodium complexes.

EXPERIMENTAL

All operations related to the synthesis and isolation of compounds were carried out under argon in dehydrated solvents. The compound $[Cp^*RhCl_2]_2$ was prepared by a reported procedure [7]. Commercial $CpMn(CO)_3$ and $W(CO)_6$ were used as received.

Synthesis of $CpFe(CO)(PPh_3)TePh$ (I). Weighed portions of $CpFe(CO)_2TePh$ (0.50 g, 1.31 mmol) and PPh_3 (0.36 g, 1.31 mmol) were dissolved in toluene (29 mL). The resulting dark green solution was magnetically stirred at reflux for 3 h with IR and TLC monitoring, then concentrated to 5 mL, and heptane (5 mL) was added dropwise before crystallization started. As the mixture was kept at –20°C for 12 h, a dark brown solid precipitated. More heptane (10 mL) was added. An oily precipitate formed, which crystallized at –20°C for 20 min. The mother liquor was removed and the brown crystals were washed with hexane and dried in vacuo. The yield was 0.40 g (50%).

IR (KBr; ν, cm^{-1}): 3446 br.w, 3057 w, 1916 vs, 1572 w, 1480 w, 1996 w, 1431 m, 1087 w, 1015 w, 997 w, 828 w, 750 w, 732 w, 694 w, 686 w, 563 w, 550 m, 527 m, 507 w, 496 w.

^1H NMR (CD_2Cl_2; δ, ppm): 4.43 C_5H_5 (d, $^3J_{P-Te}$ = 1.1 Hz), 6.97 (m, 2H), 7.14 (m, 1H), 7.75 (m, 2H) $TeC_6\boldsymbol{H}_5$, 7.36–7.56 (m, 15H, $P(C_6H_5)_3$). $^{31}P\{H\}$ (CD_2Cl_2; δ, ppm): 73.9 (s, $^2J_{P-Te}$ = 126 Hz). ^{125}Te NMR (CD_2Cl_2; δ, ppm): –275.5 (d, $^2J_{P-Te}$ = 126 Hz).

For $C_{30}H_{25}OPFeTe$		
anal. calcd., %:	C, 58.50;	H, 4.09.
Found, %:	C, 58.35;	H, 4.04.

Synthesis of $CpFe(CO)(PPh_3)(\mu\text{-}TePh)CpMn(CO)_2$ (II). THF (30 mL) was added to $CpMn(CO)_3$ (0.20 g, 0.66 mmol, excess). The yellow solution was irradiated with UV light at –20°C for 45 min; the solution color changed from yellow to bright pink. Compound **I** (0.20 g, 0.33 mmol) was added and the pink-brown solution thus formed was concentrated to dryness. The color of the precipitate turned into green upon drying. The precipitate was dissolved in CH_2Cl_2 (20 mL), the green solution was filtered and concentrated until crystallization started, heptane (5 mL) was added, and a dark green solid precipitated. Keeping of the mixture at 5°C for 30 min induced fast crystallization. The mother liquor was filtered and the dark green crystals were washed with a minimum portion of heptane and dried in vacuo. The yield was 0.21 g (82%).

IR (KBr; ν, cm^{-1}): 3441 br.w, 2924 w, 1948 vs, 1900 vs, 1839 vs, 1636 w, 1570 w, 1479 w, 1431 w, 1384 w, 1163 w, 1091 w, 1016 w, 998 w, 922 w, 841 w, 825 w, 756 w, 743 w, 698 w, 658 w, 610 w, 600 w, 588 w, 578 w, 545 w, 527 w, 506 w, 460 w, 429 w.

Synthesis of $CpFe(CO)(PPh_3)(\mu\text{-}TePh)W(CO)_5$ (III). A solution of $W(CO)_6$ (0.20 g, 0.56 mmol) in THF (22 mL) was irradiated with UV light for 1 h. Compound **I** (0.34 g, 0.56 mol) was added to the resulting solution and the mixture was stirred for 10 min. THF was removed in a water jet pump vacuum and the brown residue was triturated with hexane (10 mL). The brown powder insoluble in hexane was extracted with Et_2O (2 × 10 mL).The combined green-brown extracts were concentrated to half volume. The green crystals of unidentified complex that precipitated after 30 min at –70°C were collected on a filter, washed with heptane (2 × 2 mL), and dried in vacuo. The green crystals of complex **III** precipitated after keeping the mother liquor for 24 h at –20°C were separated by decantation, washed with pentane (2 × 5 mL), and dried in vacuo. The yield was 103 mg. An additional portion (35 mg) of complex **III** was isolated by adding hexane (4 mL) to the mother liquor and keeping the mixture at –20°C for a week. The total yield of **III** was 138 mg (25.8%).

The crystals of **III** suitable for X-ray diffraction were prepared by diffusion of hexane into a solution of **III** in CH_2Cl_2.

IR (KBr; ν, cm^{-1}): 3060 br.vw, 2060 m, 1991 m, 1952 s, 1921 vs, 1888 s, 1570 w, 1479 w, 1471 w, 1432 w, 1384 w, 1184 w, 1159 w, 1092 w, 1015 w, 1001 w, 842 vw, 826 vw, 744 vw, 735 w, 693 w, 594 w, 578 w, 547 w, 525 w, 508 vw, 460 vw, 429 vw.

^{1}H NMR ($CDCl_3$; δ, ppm): 4.47 (d, $^3J_{P-H}$ = 1.3 Hz, $C_5\boldsymbol{H}_5$), 7.6–7.0 (m, $4C_6\boldsymbol{H}_5$). ^{31}P{H} NMR ($CDCl_3$; δ, ppm): 70.6 (s, $^2J_{P-Te}$ = 81 Hz). ^{125}Te NMR ($CDCl_3$; δ, ppm): –228 (d, $^2J_{P-Te}$ = 81 Hz).

For $C_{35}H_{25}O_6PFeTeW$

anal. calcd., %:	C, 44.72;	H, 2.68.
Found, %:	C, 45.36;	H, 3.25.

Synthesis of $CpFe(CO)(PPh_3)(\mu\text{-}TePh)RhCl_2Cp^*$ (IV). A weighed portion of $[Cp^*RhCl_2]_2$ (21 mg, 0.034 mmol) was added to a brown solution of **I** (42 mg, 0.068 mmol) in CH_2Cl_2 (10 mL). After stirring for 30 min, the orange-red solution was filtered, hexane (5 mL) was added, and the solution was concentrated in vacuo to half volume. The brown-red powder resulting from keeping overnight at –20°C was collected on a filter, washed with hexane, and dried in vacuo. The yield of **IV** was 39 mg (62%).

For $C_{40}H_{40}Cl_2OPFeRhTe$

anal. calcd., %:	C, 51.94;	H, 4.36.
Found, %:	C, 51.25;	H, 6.01.

IR (KBr; ν, cm^{-1}): 3050 br.w, 2986 vw, 2960 vw, 2910 vw, 1952 vs, 1571 w, 1479 m, 1450 vw, 1433 m, 1374 w, 1183 vw, 1157 w, 1115 m, 1091 s, 1026 br.m, 847 br.w, 749 m, 698 s, 615 w, 576 w, 548 m, 527 s, 509 w, 495 vw, 461 br.w.

^{1}H NMR (C_6D_6; δ, ppm): 1.34 (s, $C_5\boldsymbol{M}$); 5.1 (d, $^3J_{P-H}$ = 0.9 Hz $C_5\boldsymbol{H}_5$), 7.1–7.28, 7.7, 8.3 (m., $4C_6H_5$). ^{31}P NMR{H} (C_6D_6; δ, ppm): 73.0 (s, $^2J_{P-Te}$ = 115.7 Hz).

The crystals of **IV** suitable for X-ray diffraction were prepared by diffusion of pentane vapor into a solution of **IV** in $CDCl_3$ at –20°C.

Elemental analysis was carried out on a Carlo Erba CHNS analyzer. IR spectra were measured on a BrukerAlpha FT IR spectrometer (KBr pellets). ^{1}H, ^{31}P{H}, and ^{125}Te NMR spectra were recorded on a Bruker AV 300 spectrometer operating at 300.21, 121.53, and 94.72 MHz, respectively, using internal deuterium lock at room temperature (298 K). The ^{1}H chemical shifts were referred to tetramethylsilane, ^{31}P chemical shifts were measured relative to external 85% H_3PO_4, and ^{125}Te chemical shifts were determined relative to external Te_2Ph_2 in $CDCl_3$ (δ = 2 ppm). The deuterated solvents were dried with 4 Å molecular sieves. The samples for NMR were prepared under argon using the standard Schlenk technique.

X-ray diffraction analysis was carried out on a Bruker APEX II CCD diffractometer. The crystallographic data and structure refinement parameters for **II–IV** are summarized in the table. The absorption corrections were applied by multiple measurements of equivalent reflections (SADABS) [8]. The structures of **II–IV** were solved by the direct method and refined by the least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms using the SHELXTL program package [9]. The H atom positions were calculated geometrically.

Crystallographic data and structure refinement details for **II**, **III**, and **IV** · $3CDCl_3$

Parameter	Value		
	II	**III**	**IV** · $3CDCl_3$
M	791.97	1024.75	924.95
Radiation (λ , Å)	MoK_α (0.71073)		
Measurement temperature, K	150(2)	173(2)	180(2)
Space group	Cc	$P\bar{1}$	$P\bar{1}$
a, Å	7.8890(13)	9.8866(11)	11.3688(7)
b, Å	18.628(3)	10.8934(12)	12.4836(8)
c, Å	21.734(4)	16.0554(18)	18.3638(1)
α, deg	90	84.952(2)	91.843(1)
β, deg	94.716(3)	74.418(2)	103.600(1)
γ, deg	90	75.121(2)	97.491(1)
V, Å^3	3183.1(9)	1609.4(3)	2506.2(3)
Z	4	2	2
$\rho_{calcd.}$, g/cm^{-3}	1.653	2.115	1.226
μ, mm^{-1}	1.837	5.175	1.351
F(000)	1576	984	920
Scanning range of θ, deg	2.19–26.33	1.32–27.92	1.14–29.00
Scan mode	ω		
Number of independent reflections (N_1)	6409 ($R_{int} = 0.0464$)	7661 ($R_{int} = 0.0294$)	13271 ($R_{int} = 0.0225$)
he number of reflections with $I > 2\sigma(I)$ (N_2)	5619	6400	10598
The number of refined parameters	398	406	429
GOOF (F^2)	1.013	0.998	0.982
R_1 for N_2	4.42	2.82	2.98
wR_2 for N_1	8.72	6.86	7.69
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.107/–1.139	0.941/–0.961	1.325/–0.555

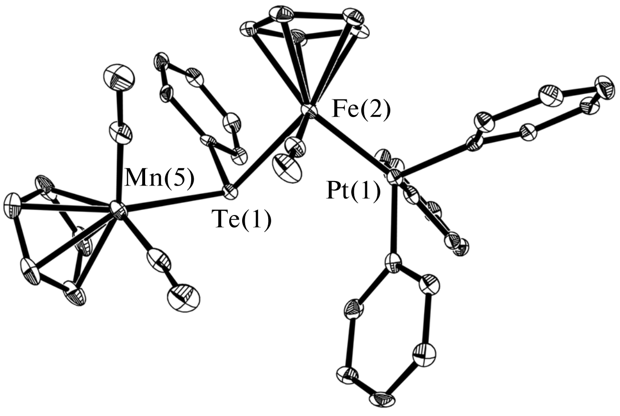


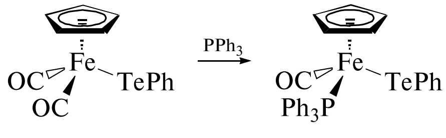
Fig. 1. Molecular structure of **II** (one of the two independent molecules is shown). Selected bond lengths and angles: Fe(2)–Te(1), 2.599(9); Fe(2)–P(1), 2.216(2); Mn(5)–Te(1), 2.559(1); Te(1)–C(8), 2.139(6) Å; P(1)Fe(2)Te(1), 92.59(5)°; C(8)Te(1)Mn(5), 106.3(2)°; C(8)Te(1)Fe(2), 102.4(2)°; Mn(5)Te(1)Fe(2), 112.34(3)°.

Selected bond lengths and bond angles in structures **II**, **III**, and **IV** · $3CDCl_3$ are given in the captions to Figs. 1–3. The structural contribution of disordered $CDCl_3$ solvate molecules in the crystal of **IV** · $3CDCl_3$ was eliminated by the SQUEEZE procedure implemented in the PLATON software [10].

Atom coordinates and other parameters for structures **II**, **III**, and **IV** · $3CDCl_3$ are deposited with the Cambridge Crystallographic Data Centre (nos. 063654, 1063655, and 1038123, respectively; http://www.ccdc.cam.ac.uk/data_request/cif).

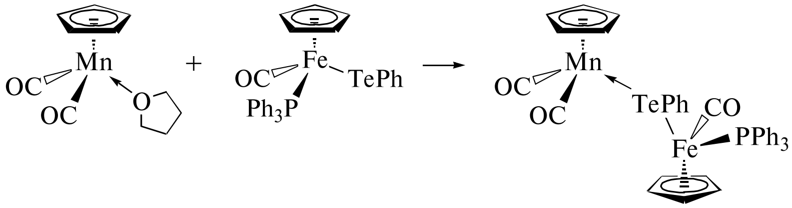
RESULTS AND DISCUSSION

The replacement of the electron-withdrawing CO group in the $CpFe(CO)_2TePh$ monomer by electron-donating PPh_3 affords **I**, which is reflected in the IR spectrum by the presence of one band (1996 cm^{-1}) instead of two bands (2017 and 1970 cm^{-1}) characteristic of stretching vibrations of terminal CO groups:



(I)

The reaction of compound **I** with $CpMn(CO)_2(THF)$, prepared by UV-irradiation of $CpMn(CO)_3$ in THF gave rise to complex **II**:



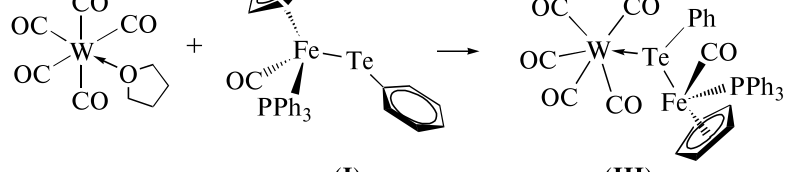
(I) **(II)**

Complex **II** is highly unstable in air both in the solid state and in solutions. On heating above 50°C, the complex decomposes. The IR spectrum in KBr exhibits CO absorption bands at 1948, 1900, and 1839 cm^{-1}, which attests to the presence of three terminal CO groups.

According to X-ray diffraction data (Fig. 1), complex **II** has Fe–Te and Mn–Te bonds (2.599(9) and 2.559(10) Å, respectively) that are substantially shorter than the sums of covalent radii (2.70 and 2.77 Å, respectively [11]) owing to the additional $M \to$ Te dative interaction.

Note that two asymmetric centers appear in **II**, namely, iron and tellurium atoms, resulting in the formation of diastereomers. Unfortunately, due to instability, this complex cannot be studied by NMR in solutions.

Complex **I** readily reacts with $W(CO)_5THF$ prepared photochemically from tungsten carbonyl. In this reaction, the THF molecule at the tungsten atom is replaced giving new heterometallic complex **III**:



(I) **(III)**

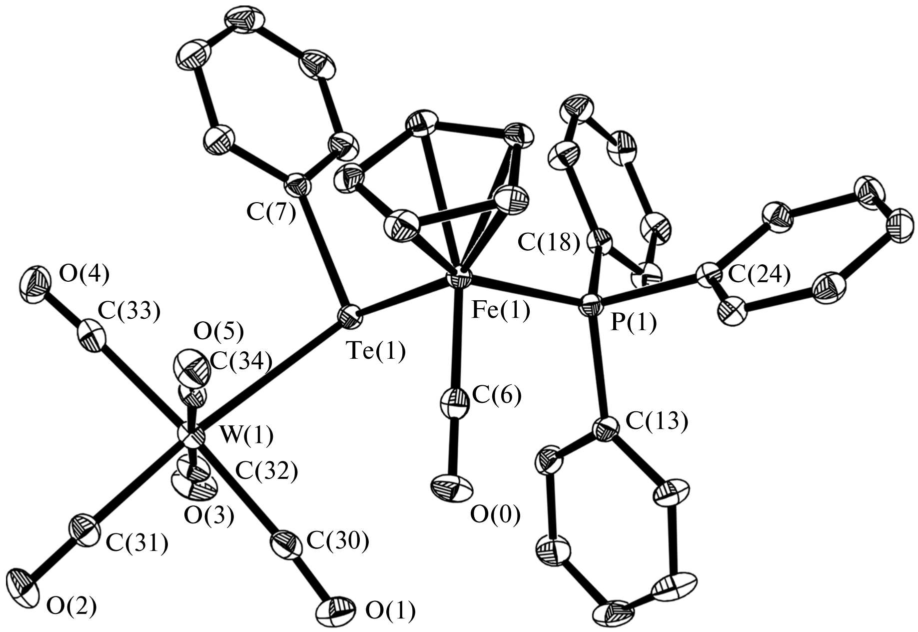
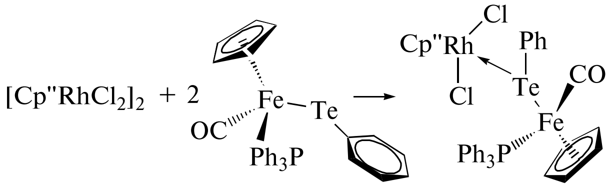


Fig. 2. Molecular structure of **III**. Selected bond lengths and angles: W(1)–Te(1), 2.8489(4); Fe(1)–Te(1), 2.5968(6); Fe(1)–P(1), 2.230(1); W(1)–C(34), 2.035(4); W(1)–C(32), 2.037(5); W(1)–C(30), 2.035(5); W(1)–C(33), 2.042(5); W(1)–C(31), 1.976(4) Å; Fe(1)Te(1)W(1), 110.98(1)°; C(7)Te(1)Fe(1), 103.3(1)°.

The IR spectrum of **III** in KBr contains four bands in the range of CO stretching modes of the $W(CO)_5$ moiety (2060, 1991, 1952, and 1921 cm^{-1}), which is apparently related to non-equivalence of the equatorial CO groups in the crystal, and one band for **I** (at 1888 cm^{-1}). Complexing with the tungsten moiety induces a downfield shift of the Te signal in the ^{125}Te NMR spectrum (–228 ppm) with respect to this signal for initial **I** (–275.5 ppm). Also, the spin–spin coupling constant $^2J_{Te-P}$ decreases substantially from 126 to 81 Hz, althogh the geometry of the ligand environment of iron changes onlu slightly.

The structure of **III** was established by X-ray diffraction (Fig. 2). The Fe–Te bond in the complex (2.5968(6) Å) is somewhat shorter than that in $CpFe(CO)_2TePh$ (2.617 Å) [12], whereas in the thiolate-bridged complex $CpFe(CO)_2(\mu\text{-}SPh)W(CO)_5$, coordination of the second metal atom results in elongation of the Fe–S bond (2.31 Å) [13] compared to that in $CpFe(CO)_2SPh$ (2.28 Å) [14]. The W–Te bond length in **III** is 2.8489(4) Å, both *M*–Te bonds being shorter than the sums of the covalent radii ($r_{Fe} + r_{Te} =$ 2.70 Å, $r_W + r_{Te} = 3.00$ Å) [11], probably, due to the additional dative interaction of the metal lone pairs with the tellurium vacant orbitals.

The addition of **I** as the ligand to the rhodium atom easily proceeds upon dissociation of the dimer $[Cp^*RhCl_2]_2$ in dichloromethane without any heating and results in the formation of brown-red crystals of complex **IV**, which gives rise to only one stretching band for the terminal CO group in the IR spectrum (1952 cm^{-1}).



(I) **(IV)**

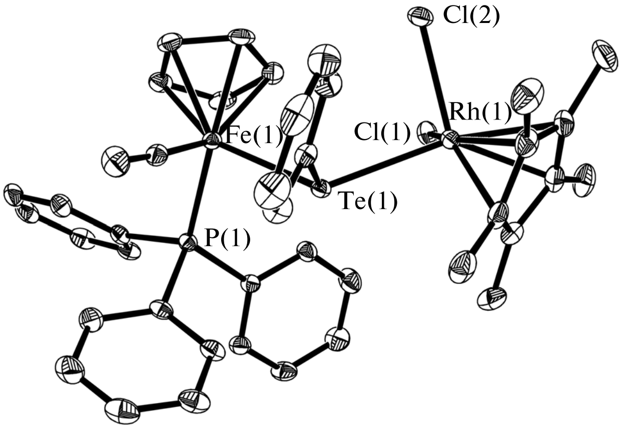


Fig. 3. Molecular structure of **IV**. Selected bond lengths and angles: Te(1)–Fe(1), 2.5644(4); Te(1)Rh(2), 2.6883(2); Te(1)–C(7), 2.137(2); Fe(1)–P(1), 2.2318(6) Å; Fe(1)Te(1)Rh(2), 124.27(1)°, C(7)Te(1)Fe(1), 101.57(6)°.

The structure of **IV** · $3CDCl_3$ was established by X-ray diffraction (Fig. 3). The metal atoms are connected by only one tellurophenyl bridge, and the Te–Fe and Te–Rh bonds (2.5644(4) and 2.6883(2) Å, respectively), like these bonds in other heterometallic complexes, are much shorter than the sum of the covalent radii (2.70 and 2.80 Å, respectively [11]) due to the additional $M \rightarrow$ Te dative interaction. The Te(1)–C(7) bond length (2.137(2) Å) is equal to the sum of the covalent radii (2.12 Å) [11], i.e., it is a single bond.

Thus, complex **I** containing asymmetric iron atom can function as a ligand in manganese, tungsten, and rhodium organometallic complexes (**II**, **III**, and **IV**), being coordinated via the tellurophenyl bridge with strongly shortened *M*–Te bonds, thus giving diastereomeric heterometallic complexes.

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