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Neodymium(II) and Dysprosium(II) Iodides in the Reactions with Metallocenes of d-Transition Metals

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Heating NdI_2 (**1**) or DyI_2 (**2**) with vanadocene (**3**) in benzene at 85 °C led to the formation of bis(benzene)vanadium in 10 and 24 % yields, respectively. The lanthanide products were isolated in the form of $CpLnI_2(THF)_3$ after crystallization from THF. The interaction of **2** with **3** in isopropylbenzene at 90 °C yielded a mixture of $(arene)_2V$ complexes from which a small amount of bis(isopropylbenzene)vanadium was isolated. The same reaction did not occur in mesitylene. From the reaction of **2** with **3** in molten naphthalene at 100 °C, the heterobimetallic cluster $\{[CpDy(\mu\text{-}I)_2]_7Cp_2V(\mu\text{-}I)\}$(**4**) was isolated in low yield. The reaction of Cp_2Cr with **1** or **2** in benzene at ambient temperature afforded the dimer $[CpCr(\mu\text{-}I)]_2$ (**5**) and a dysprosium complex, Cp_2DyI (**6**) (in the reaction with **2**). When the reaction with **2** was carried out at 80 °C, along with compound **6**, the -ate complex $\{[Cp_2DyI_2]^-[Cp_2Cr]^+\}$(**7**) was crystallized from the reaction solution. Nickelocene was reduced by **2** in benzene at 80 °C to nickel metal. The dysprosium product was isolated as solvent-free complex **6**. Ferrocene and cobaltocene did not react with **1** and **2** in benzene. The molecular structures of compounds **4**, **5**, and **7** were characterized by X-ray diffraction analysis.

Introduction

The diiodides NdI_2 (**1**), DyI_2 (**2**), and TmI_2, which recently became available for broad chemical investigations, have proven themselves as powerful reducing reagents in reactions with various organic substrates.[1] The reactivity of these salts towards organometallic compounds has been studied. Most of the examples are metathesis reactions of TmI_2 with alkali-metal derivatives to give the corresponding divalent thulium complexes, $R_2Tm(solv.)_n$, or the products of their oxidation by the solvent and disproportionation.[2] The reactions of LnI_2 with RM {R = 2,6-tBu$_2$C$_6$H$_3$O,[3] $[(Me_3Si)_2]_2N$,[3] C_5Me_5,[2b] $(Me_3Si)C_5H_4$,[2b] $(Me_3Si)_2C_5H_3$;[2a,2b] M = Na, K} in THF or ether, conducted in nitrogen, yielded the corresponding nitrogen-containing complexes of the type $[(R_2Ln)_2(\mu_2\text{-}N_2)]$. The addition of Ph_2Hg, Ph_3GeH, $Ph_3GeGePh_3$, or Ph_4Sn to a solution of **1** or **2** in THF caused the formation of the triiodide $LnI_3(THF)_3$ and a mixture of monoiodide complexes of the type LnIRR′ containing fragments of split solvent.[4,5] Reaction of **1** with Me_3SiCl in THF proceeds vigorously to give Me_3SiH, $Me_3SiSiMe_3$, and Me_3SiOBu.[6] Pentafluorophenyl germanes $(C_6F_5)_3GeH$ and $(C_6F_5)_3GeBr$ react with **1** in THF to produce a hyperbranched polymer $[(C_6F_5)_2Ge(C_6F_4)]_n$.[5] The reactivity of **1** and **2** (as well as all other LnI_2) towards organometallic compounds of d-transition metals has never been studied. In an effort to fill this gap, we have investigated the reactions of **1** and **2** with metallocenes of vanadium, chromium, iron, cobalt, and nickel. The second aim of this work was to develop a new way to arene complexes of these metals; therefore, the reactions were carried out in aromatic solvents. Neodymium and dysprosium diiodides were selected because they are the most active reductants among all the LnI_2.

Results and Discussion

The main preparative route to bis(arene) complexes of d-transition metals is still Fischer's method – the reflux of a mixture of the metal halide, $AlCl_3$, and aluminum powder in the appropriate aromatic solvent and subsequent hydrolysis of the formed intermediates.[7] We have found that bis(benzene)vanadium can be obtained by the reaction of **1** or **2** with vanadocene (**3**) in benzene at 80 °C.[8] When the mixture was heated for 10 h, the yield of $(C_6H_6)_2V$ was 10% for **1** and 24% for **2**. An increase in reaction time did not lead to greater yields of bis(benzene)vanadium. Changing the molar ratio **2/3** from 2 to 4 increased the yield of $(C_6H_6)_2V$ from 15% to 24%. Despite a great excess of LnI_2 most of the vanadocene could be isolated from the reaction mixture. This can be explained by the heterogeneous nature of the processes: the formed lanthanide product $CpLnI_2$, sparingly soluble in benzene, covers the surface of iodide **2** and prevents it from reacting further with **3**. The neodym-

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ium derivative has especially low solubility; therefore, only a few crystals of it were isolated as the solvated $CpNdI_2(THF)_3$ after crystallization from THF.

$$2\,LnI_2 + Cp_2V \xrightarrow{\text{benzene}} (C_6H_6)_2V + 2\,CpLnI_2$$
$$Ln = Nd, Dy$$

An attempt to use VCl_4 instead of **3** in this synthesis failed: the reduction of vanadium with **2** proceeds rapidly but stops at the formation of the benzene-insoluble VCl_3.

The mechanism of $(C_6H_6)_2V$ formation from **3** and LnI_2 remains unclear, but taking into account the generation of lanthanide–naphthalene–vanadium(0) complexes $[CpLn(THF)(\mu\text{-}C_{10}H_8)VCp]_n$ (Ln = Sm, Eu, Yb)[9] or the triple-decker vanadium compound $CpV(\mu\text{-}C_{10}H_8)VCp$[9a] in the reactions of **3** with other strong reductants such as lanthanide(II) naphthalenides $(C_{10}H_8)Ln(THF)_x$ suggests that reduction of **3** by **1** and **2** also proceeds via intermediates of the type $CpV(\mu\text{-}C_6H_6)LnI_2$, probably generated on a surface of LnI_2. However, in the reaction of **2** with **3** in molten naphthalene, where the formation of naphthalene–vanadium derivatives seemed very plausible, we were unable to isolate any arene–vanadium product although almost all of the vanadocene was consumed. The reaction readily proceeds at 100 °C to give a black solution from which only heterobimetallic cluster **4** has been isolated by crystallization from benzene. The black insoluble pyrophoric precipitate, remaining after the removal of the reaction solution, contained (according to elemental analysis and IR spectroscopy) dysprosium, vanadium, cyclopentadienyl, and arene groups. This is consistent with above supposition. Note that naphthalene–ytterbium, –samarium, and –europium are also pyrophoric.

The molecule **4** (Figure 1) is a bimetallic polynuclear complex. The metal atoms [Dy(1–3), V(1) and Dy(4–7)] are positioned at the apexes of distorted tetrahedrons and are bonded to each other by the bridging iodine atoms that form a distorted octahedron around each dysprosium atom. The iodine atoms occupy equatorial positions and the one apical position inside the cluster. The apical positions outside of the cluster are occupied by Cp ligands. The Dy(1–3) atoms, μ_2-I [I(12), I(13), and I(23)] atoms, and the μ_3-I(123), and μ_3-I(321) atoms are located at the apexes of a distorted hexagonal bipyramid. The deviation of the Dy(1–3) and I (12, 13, and 23) atoms from the plane are 0.079 Å. The Dy(1–3)–μ_2-I distances in the Dy(1–3),V(1) metallofragment vary in the range 3.0568(4)–3.1269(4) Å and are shorter than the Dy(1–3)–μ_3-I distances [3.1544(4)–3.2248(4) Å]. The Dy(4, 6, 7), I(47, 67, 456) (planar location) and I(467, 654) (apical location relative to the plane) atoms in the Dy(4–7) metallofragment are also located at the apexes of a distorted hexagonal bipyramid. However there is a significant difference between the Dy(4, 6, 7)–I(47, 67, 456,467, 654) and Dy(1–3)–I (12, 13, 23, 123, 321) fragments of the cluster. The Dy(5) atom in the Dy(4, 5, 6, 7) fragment is positioned under the I(456)···I(654) edge and it interacts with these iodine atoms, whereas the vanadium atom has no additional V–I interactions. As a result, the I(654) atom is a bridging four-coordinate atom. The Dy(5, 7)–μ_4-I(654) distances [3.3609(4), 3.3381(4) Å] are significantly longer than the Dy(4–7)–μ_2-I [3.0407(4)–3.1261(5) Å] and Dy(4–7)–μ_3-I [3.1420(4)–3.1816(5) Å] distances. It should be noted that the Dy(4, 6)–μ_4-I(654) bonds [3.2191(4) and 3.2406(4), respectively] are shorter than the Dy(5, 7)–μ_4-I(654) bonds. The Dy–Cp_{center} and V–Cp_{center} distances vary in the range 2.309(6)–2.331(6) Å and 1.934(6)–1.939(6) Å, respectively, and are typical for similar fragments ($[Cp_2DyBr]_2$, 2.327–2.360 Å;[10] Cp_2V, 1.918 Å;[11] Cp_2VCl, 1.944, 1.946 Å[12]).

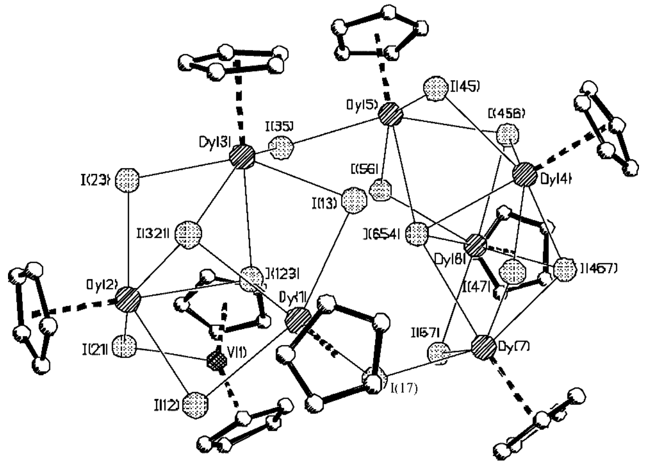

Figure 1. Molecular structure of $\{[CpDy(\mu\text{-}I)_2]_7Cp_2V(\mu\text{-}I)\}$ (**4**). Hydrogen atoms have been omitted for clarity. Relevant bond lengths [Å] and angles [°]: Dy(1)–I(12) 3.1077(4), Dy(1)–I(13) 3.0568(4), Dy(1)–I(17) 3.1451(4), Dy(1)–I(123) 3.1544(4), Dy(1)–I(321) 3.2248(4), Dy(1)–C(11–15) 2.592(5)–2.609(5), Dy(7)–I(17) 3.0583(4), V(1)–I(21) 2.8203(10), V(1)–I(1–10) 2.259(6)–2.297(6); I(13)–Dy(1)–I(12) 149.595(12), I(13)–Dy(1)–I(17) 95.692(12), I(12)–Dy(1)–I(17) 92.424(12), I(12)–Dy(1)–Cp_{center} 103.5, Cp_{center}–V(1)–Cp_{center} 142.3, I(21)–V–Cp_{center} 108.6 (109.0).

No changes were observed when a mixture of **2** and **3** was heated in mesitylene at 90 °C. The same reaction in isopropylbenzene afforded a mixture of bis(arene)vanadium complexes [arene = C_6H_6, $C_6H_5C_3H_7$, $C_6H_4(C_3H_7)_2$] isolated as a dark brown oily liquid. A similar mixture of arene–vanadium products is formed in the reaction of VCl_3 with $AlCl_3$ and Al in $i\text{-}C_3H_7C_6H_5$.[13] From the reaction mixture, we were able to isolate a small amount of bis(isopropylbenzene)vanadium as yellow crystals.

Chromocene reacted with **1** in benzene at ambient temperature but did not give the expected bis(benzene)chromium. Instead, from the cherry solution, the dimer **5** was isolated as an air-sensitive, dark cherry-red crystalline solid soluble in benzene and hexane. Single crystals of **5** suitable for X-ray analysis were obtained by crystallization from hexane.

The centrosymmetric molecule **5** (Figure 2) consists of two CpCrI fragments bonded by iodine bridges. The four-membered Cr(1)I(1)Cr(1A)I(1A) cycle has a butterfly shape characteristic of similar fragments.[14] The dihedral angles between the Cr(1)I(1)I(1A) and Cr(1A)I(1)I(1A) fragments is 87.6°. The Cr(1)–I and Cr(1)–C(Cp) distances are 2.6678(5)–2.6592(5) Å and 2.242(2)–2.295(2) Å, respectively, and are typical for the same type of complexes [2.671–2.707 Å for Cr–μ-I and 2.192–2.241 Å[15] for Cr–C(Cp)]. A short Cr···Cr contact [2.4921(7) Å] in the molecule indicates the existence of bonding between the two metal atoms. Similar Cr–Cr bonding has been found before in the complexes [Cp*Cr(μ-Cl)]$_2$ [2.642(2) Å], [Cp*Cr(μ-Me)]$_2$ [2.263(3) Å], and [(Cp*Cr)$_2$(μ-Me)(μ-Ph)] [2.289(4) Å].[14]

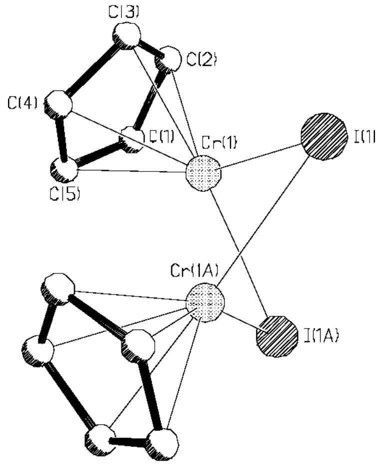

Figure 2. Molecular structure of [CpCr(μ-I)]$_2$ (**5**). Hydrogen atoms have been omitted for clarity. Relevant bond lengths [Å] and angles [°]: Cr(1)–Cr(1A) 2.4921(7), Cr(1)–I(1) 2.6678(5), Cr(1A)–I(1) 2.6592(5), Cr(1)–C(Cp) 2.242(2)–2.295(2); Cr(1A)I(1)Cr(1) 55.787(2), I(1A)Cr(1)I(1) 94.905(2).

Increasing the reaction temperature to 80 °C did not lead to the formation of $(C_6H_6)_2Cr$. In this case, extensive transformations resulted in the formation of a green intractable mixture from which no definite products were isolated.

Similar to the neodymium salt, dysprosium iodide (**2**) reacted with Cp_2Cr in benzene at room temperature to give dimer **5** and dysprosium(III) complex **6**. When the reaction was carried out at 80 °C the dimer **5** was not found in the mixture but product **6** was isolated in 34% yield. Its formation was confirmed by elemental analysis and IR spectroscopic data; however, the single crystal selected for X-ray diffraction analysis quite unexpectedly turned out to be the -ate complex {$[Cp_2DyI_2]^-[Cp_2Cr]^+$}(**7**), which can be considered as a combined product of Cp_2DyI and Cp_2CrI.

According to X-ray data, molecule **7** contains the counterions $[Cp_2DyI_2]^-$ and $[Cp_2Cr]^+$ (Figure 3). The dysprosium and chromium atoms are located on the C_2 axis and the mirror plane, respectively. The bond angles Cp_{cent}–Dy(1)–Cp_{cent} and I(1)–Dy(1)–I(1A) are 128.3 and 95.4°, respectively, and the distances Dy(1)–C(Cp) and Dy(1)–I vary in the ranges 2.615(4)–2.648(4) Å and 2.9818(5)–2.9926(5) Å, respectively. The Dy(1)–C(Cp) bond length in **7** is similar to the bond lengths in **4** [2.566(6)–2.637(6) Å] but the Dy–I bonds in **7** are somewhat shorter than the analogous bonds in **4**. The shortening of the Dy–I bonds in **7** probably reflects a different type of coordination of the iodine atoms in these two compounds. The iodine atoms in **7** are terminal, whereas all I atoms in **4** are bridging. The $[Cp_2Cr]^+$ cation has an ordinary geometry. To the best of our knowledge, the structure of only one complex containing the $[(Me_5C_5)_2LnI_2]^-$ anion (Ln = Yb) has been published previously.[16]

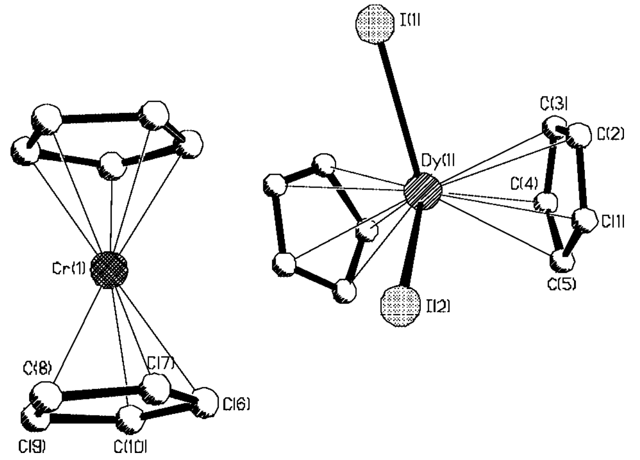

Figure 3. Molecular structure of $[Cp_2DyI_2]^-[Cp_2Cr]^+$ (**7**). Hydrogen atoms have been omitted for clarity. Relevant bond lengths [Å] and angles [°]: Dy(1)–I(1) 2.9926(5), Dy(1)–I(2) 2.9818(5), Dy(1)–C(Cp) 2.615(4)–2.648(4), Cr(1)–C(Cp) 2.188(4)–2.201(4); I(1)–Dy(1)–I(2) 95.41(1), Cp_{center}–Dy–Cp_{center} 128.3, Cp_{center}–Cr–Cp_{center} 179.0.

The only definite product isolated from the reaction of **2** with nickelocene in benzene at 80 °C was the dysprosium(III) complex **6**. Reduced nickel was deposited as a mirror on the walls of the reaction flask.

No transformations were observed when Cp_2Fe and Cp_2Co were heated with **1** or **2** in benzene at 80 °C for 10 h. Interestingly, addition of Cp_2Fe to a THF solution of **2** caused immediate formation of DyI_3 and DyIRR' (R,R′ = fragments of THF). Ferrocene was isolated unchanged from the reaction mixture. As it was mentioned above, similar transformations have been observed before in the reactions of **1** and **2** with aromatic compounds or phenyl derivatives of mercury, germanium and tin in THF or DME.[4]

Conclusions

The study revealed that the iodides **1** and **2** could react with metallocenes of vanadium, chromium, and nickel in nonsolvating aromatic solvents, but only in the reactions with vanadocene in benzene was the expected bis(arene) complex obtained in noticeable amounts indicative of the redox character of the transformations. In all other cases, the isolated products $CpLnI_2$, **4**, **5**, and **7** were arene-free. Formation of dimer **5** and cluster **4** reveals that most of these reactions are accompanied by Cp/I exchange. Ferrocene and cobaltocene turned out to be inert toward iodides **1** and **2** in benzene.

Experimental Section

General Remarks: All procedures were performed under vacuum using standard Schlenk-tube techniques. Benzene, cumene, and mesitylene were dried by refluxing over sodium and treated with **1** for 30 min before use. Diiodides **1** and **2** were purchased from Synor

(Nizhny Novgorod) and used without additional purification. Vanadocene and cobaltocene were prepared according to published procedures.[17,18] Ferrocene, nickelocene, and chromocene were purchased from Aldrich. The ESR spectra were recorded with a Bruker 200D-SRC instrument. The IR spectra of the samples, prepared as Nujol mulls, were recorded with a Specord M-75 spectrometer. Melting points were determined in sealed capillaries.

Reaction of DyI_2 (2) with Cp_2V (3) in Benzene: A solution of **3** (0.2 g, 1.10 mmol) in benzene (10 mL) was added to a powder of **2** (1.89 g, 4.54 mmol), and the mixture was stirred at 80 °C for 10 h. The resultant dark brown solution was separated from the precipitate by decantation, the solvent was removed by evaporation in vacuo, and the residue was extracted with hexane (2 × 10 mL). The extract was placed into an apparatus for sublimation, hexane was evaporated in vacuo, and the solid residue was heated gradually up to 110 °C. The sublimed mixture of violet and dark brown crystals was sublimed again. At 50–60 °C (0.1 Torr) violet crystals of **3** (0.11 g, 54%) were collected and separated [ESR (77 K): $g_{\perp} = 4.0$, $A_{\perp}$ (^{51}V) = 2.8 mTs, $g = 2.0$]. Sublimation of the remaining substance at 100–110 °C (0.1 Torr) gave dark brown crystals of $(C_6H_6)_2V$. Yield 55 mg (24%); m.p. 275–277 °C; ESR (293 K): $A_i(^{51}V) = 6.35$ mT, $g_i = 1.986$. The solid residue after extraction with hexane was recrystallized from THF to give $CpDyI_2(THF)_3$ (75 mg, 5%). Decomposition temperature, IR spectrum and results of elemental analysis of the product were identical to those of the previously synthesized compound.[19]

Reaction of NdI_2 (1) with Cp_2V (3) in Benzene: Compound **1** (3.46 g, 8.69 mmol) reacted with compound **3** (0.35 g, 1.93 mmol), under the conditions of the previous experiment, to give $(C_6H_6)_2V$ (42 mg, 10%). The sublimation of the solid products gave unreacted **3** (0.24 g, 69%). From the solid residue after hexane extraction, a few crystals of $CpNdI_2(THF)_3$ were isolated by recrystallization from THF. Characteristics of the product were identical to those of the complex obtained in the reaction of **1** with cyclopentadiene.[19]

Reaction of DyI_2 (2) with Cp_2V (3) in Isopropylbenzene: A mixture of **2** (1.01 g, 2.43 mmol), **3** (0.2 g, 1.11 mmol), and isopropylbenzene (7 mL) was stirred at 90 °C for 20 h. The resultant red-brown solution was separated from the precipitate by decantation, and cumene was removed in vacuo. A waxy residue was extracted with hexane (10 mL), and the extract was transferred into a sublimation apparatus. After evaporation of hexane, the solid products were sublimed in vacuo by gradually increasing the temperature from 20 °C to 150 °C. Unreacted **3** (57 mg, 29%), which sublimed at 50–60 °C, was collected in the top part of the apparatus. At 100–120 °C, yellow needle crystals of $(iPrC_6H_5)_2V$ (4 mg, 1%) sublimed; ESR (300 K): $a_i(^{51}V) = 6.29$ mT, $g_i = 1.988$, $A_i(H) = 5$ G.

Reaction of DyI_2 (2) with Cp_2V (3) in Naphthalene: A mixture of **2** (1.6 g, 3.84 mmol), **3** (0.26 g, 1.44 mmol), and naphthalene (2.5 g) was stirred at 110–120 °C in a sealed ampoule. After 20 h, the resultant black mixture was cooled to room temperature to give a black solid from which a mixture of naphthalene and unreacted **3** was separated by sublimation in vacuo at 50–60 °C. The black residue was extracted with benzene (3 × 30 mL), the greenish solution obtained was concentrated to 8 mL and cooled to 8–10 °C to give violet crystals of **4**. The product was separated by decantation and dried in vacuo at room temperature. A sample of **4** isolated under these conditions contained three molecules of benzene. Yield 0.28 g (5%); m.p. >240 °C (dec.). $C_{63}H_{63}Dy_7I_{15}V$ (3910.94): calcd. C 19.20, H 1.81; found C 19.33, H 1.61. IR (nujol, KBr): $\tilde{\nu}$ = 1010 (s), 796 (s), 673 (m) cm^{-1}. The black residue after separation of the benzene extract was dried in vacuo at room temperature to give a black pyrophoric powder (1.35 g). IR (nujol, KBr): $\tilde{\nu}$ = 1600 (w), 1011 (m), 842 (sh), 800 (s), 677 (w), 619 (w) cm^{-1}.

Reaction of NdI_2 (1) with Cp_2Cr in Benzene (at 20 °C): A solution of Cp_2Cr (0.34 g, 0.19 mmol) in benzene (10 mL) was added to a powder of **1** (1.53 g, 0.38 mmol), and the mixture was stirred for 10 h at ambient temperature. The resultant dark-cherry solution was separated from the precipitate, and the solvent was removed in vacuo. The waxy residue was extracted with hexane (2 × 10 mL). Slow evaporation of hexane from the extract afforded **5** (0.18 g, 39%) as dark cherry-red crystals with m.p. 84–87 °C (dec.). $C_{10}H_{10}Cr_2I_2$ (487.90): calcd. C 24.60, H 2.05, Cr 21.32; found C 25.01, H 2.50, Cr 21.05. IR (nujol, KBr): $\tilde{\nu}$ = 3088 (w), 1011 (s), 815 (s), 784 (s), 720 (m), 665 (m), 561 (m) cm^{-1}.

Reaction of DyI_2 (2) with Cp_2Cr in Benzene (at 20 °C): Under the conditions of the previous experiment, compound **2** (1.12 g, 2.69 mmol) was treated with Cp_2Cr (0.24 g, 1.32 mmol) in benzene (8 mL). The resultant dark-cherry solution was separated from the precipitate, the solvent was removed in vacuo, and the residue was extracted with pentane. Cooling the extract to 0 °C gave **5** (0.142 g, 44%). The residue after pentane extraction was recrystallized from toluene to give **6** (0.146 g, 26%) as light yellow crystals. $C_{10}H_{10}DyI$ (739.02): calcd. Dy 38.74; found Dy 38.72. IR (nujol, KBr): $\tilde{\nu}$ = 1008 (s), 890 (w), 781 (s), 727 (m), 661 (m) cm^{-1}.

Reaction of DyI_2 (2) with Cp_2Cr in Benzene (at 80 °C): A mixture of **2** (0.537 g, 1.29 mmol) and Cp_2Cr (0.14 g, 0.77 mmol) in benzene (8 mL) was stirred at 80 °C for 12 h. The initial orange-red color of the solution gradually turned pale green. The solution was decanted from the black precipitate, and the solvent was evaporated in vacuo to leave behind a greenish powder, which was extracted with toluene. Cooling of the toluene extract in a refrigerator yielded yellow crystals of **6** (92 mg, 34%). $C_{10}H_{10}DyI$ (739.02): calcd. C 26.61, H 2.38, Dy 38.74; found C26.35, H 2.56, Dy 38.56. The IR spectrum was identical to that of the compound from the previous experiment. Among the isolated yellow crystals of **6**, a few greenish-yellow crystals were found. X-ray diffraction investigation of one of them revealed the compound to be -ate complex **7**. The amount of isolated **7** was not enough for elemental and spectroscopic analyses.

Reaction of DyI_2 (2) with Cp_2Ni in Benzene: A solution of Cp_2Ni (0.12 g, 0.64 mmol) in benzene (15 mL) was added to a powder of **2** (0.56 g, 1.34 mmol), and the mixture was stirred at 70 °C for 12 h. Formation of a nickel mirror on the walls of the reactor was observed. The resultant wine-colored solution was separated from the precipitate, and the latter was washed with benzene (15 mL). The reaction solution and benzene wash were combined, and the solvent was evaporated in vacuo. The solid residue was recrystallized from benzene to give **6** (0.11 g, 42%).

X-ray Diffraction Study: The X-ray diffraction data were collected with a SMART APEX diffractometer (graphite-monochromated, Mo-K_{α}-radiation, φ-ω-scan technique, $\lambda = 0.71073$ Å). The intensity data were integrated by the SAINT program.[20] SADABS[21] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and refined on F_2 using all reflections with the SHELXTL package.[22] All non-hydrogen atoms were refined anisotropically. The H atoms in **5** and **7** [except H(2)] were found from Fourier synthesis and refined isotropically. The H atoms in **4** and the H(2) atom in **5** were placed in calculated positions and refined in the "riding-model". In the unit cell of **4** were found the solvated molecules of benzene. The details of crystallographic, collection, and refinement data for **4**, **5**, and **7** are shown in the Table 1. The selected geometric characteristics for **4**, **5**, and **7** are given in the captions to Figure 1, Figure 2,

Table 1. The details of crystallographic, collection, and refinement data for **4**, **5**, and **7**.

	4	**5**	**7**
Empirical formula	$C_{69}H_{69}Dy_7I_{15}V$	$C_{10}H_{10}Cr_2I_2$	$C_{20}H_{20}CrDyI_2$
Formula mass	3990.18	487.98	728.66
Temperature [K]	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P21/n$	$C2/c$	C2/m
a [Å]	17.9963(9)	15.562(2)	15.632(1)
b [Å]	25.845(1)	6.9458(11)	16.618(1)
c [Å]	19.965(1)	12.763(2)	8.2121(5)
β [°]	105.674(1)	111.680(3)	102.599(1)
Volume [Å^3]	8940.5(8)	1282.0(3)	2081.8(2)
Z	4	4	4
Density (calculated) [g cm^{-3}]	2.964	2.528	2.325
Absorption coefficient [mm^{-1}]	11.086	6.472	7.048
$F(000)$	7052	896	1344
Crystal size [mm]	0.15 × 0.12 × 0.10	0.16 × 0.12 × 0.08	0.07 × 0.07 × 0.03
θ_{max} range for data collection [°]	25.00	29.00	25.00
Index ranges	$-21 \le h \le 21$ $-30 \le k \le 30$ $-23 \le l \le 23$	$-21 \le h \le 15$ $-9 \le k \le 7$ $-16 \le l \le 17$	$-18 \le h \le 18$ $-19 \le k \le 19$ $-9 \le l \le 9$
Reflections collected	70375	4506	8265
Independent reflections	15743 (R_{int} = 0.0400)	1696 (R_{int} = 0.0158)	1910 (R_{int} = 0.0295)
Absorption correction	SADABS		
Max/min transmission	0.4036/0.2871	0.6255/0.4241	0.8164/0.6382
Refinement method	full-matrix least squares on F^2		
Data/restraints/parameters	15743/31/829	1696/0/84	1910/2/150
Goodness-of-fit on F^2	1.118	1.099	1.085
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0261 wR_2 = 0.0609	R_1 = 0.0209 wR_2 = 0.0461	R_1 = 0.0287 wR_2 = 0.0673
R indices (all data)	R_1 = 0.0297 wR_2 = 0.0622	R_1 = 0.0245 wR_2 = 0.0473	R_1 = 0.0342 wR_2 = 0.0690
Largest difference peak/hole [e·Å^{-3}]	1.835/–1.124	0.999/–0.405	1.388/–0.621

and Figure 3. CCDC-275720 (**4**), 275721 (**5**), and 275722 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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