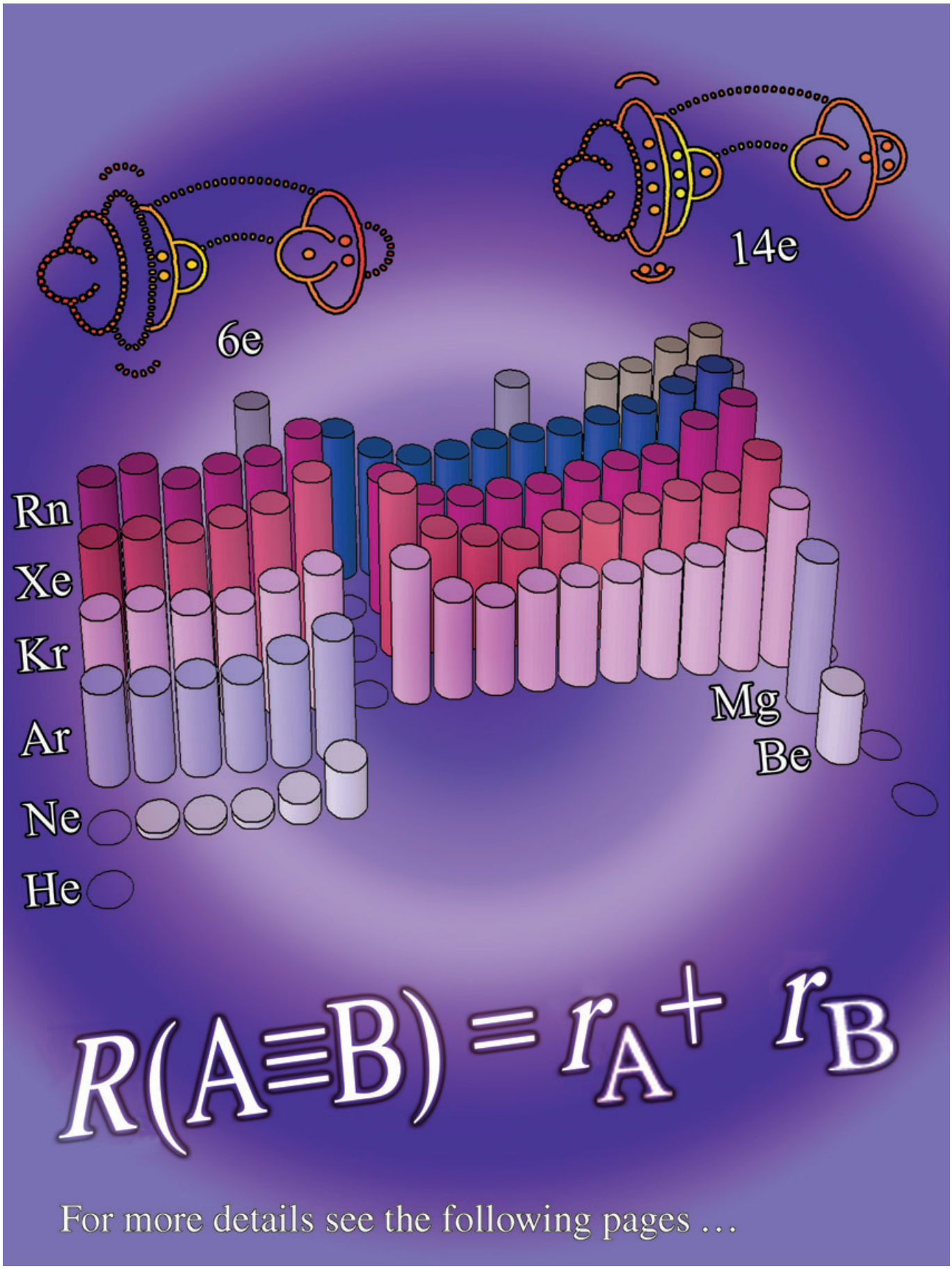

 DOI: 10.1002/chem.200401299

CHEMISTRY
A EUROPEAN JOURNAL

Triple-Bond Covalent Radii

Pekka Pyykkö,*[a] Sebastian Riedel,[a, b] and Michael Patzschke[a]

Abstract: A system of additive covalent radii is proposed for $\sigma^2\pi^4$ triple bonds involving elements from Be to E112 (eka-mercury). Borderline cases with weak multiple bonding are included. Only the elements in Group 1, the elements Zn–Hg in Group 12 and Ne in Group 18 are then totally excluded. Gaps are left at late actinides and some lanthanides. The standard deviation for the 324 included data points is 3.2 pm.

Keywords: ab initio calculations · covalent radii · density functional calculations · heavy metals · superheavy elements · triple bonds

Introduction

The aim of additive covalent radii is to express approximately, as given in Equation (1), a bond length as the sum of two atomic radii.

$$R_{AB} = r_A + r_B \quad (1)$$

A well-known source for such covalent radii for single bonds are the books by Pauling.[1,2] A more recent list is the VCH periodic table.[3]

In simple terms, the single bond corresponds to a σ^2 electron pair in a bonding molecular orbital, as in H_2, or to a corresponding net excess, as in Cl_2. Perhaps the best-defined multiple bond is a $\sigma^2\pi^4$ triple bond. No comprehensive sets of pruned triple-bond covalent radii seem to exist. In the 2nd Edition of *The Nature of the Chemical Bond*, Pauling gave three primary radii (for C, N and P) and further estimates for four other elements (B, O, Si, S).[1] In the 3rd Edition, he only kept four of them (C, Si, P, S). We now report triple-bond covalent radii for the elements from Be to E112, only excluding the alkalis, the lighter Group-12 elements (Zn–Hg) and Ne. In addition, gaps are left among the lanthanides, and the late actinides Pu–Lr are omitted. Unlike in the systems of ionic radii—since the times of Bragg[4] or Wasastjerna[5]—in which a particular radius, like that of an oxide or fluoride ion, is held fixed, the present system is self-consistent. The homonuclear systems do introduce a certain emphasis for radii included in them (see Computation Details, Equation (3)).

Furthermore, we look for a single radius for all oxidation states and coordination numbers of the elements considered. The other option would be to introduce a separate radius for each of them, as done by Shannon and Prewitt for ionic radii.[6,7]

When is a bond a triple bond? Claims for a triple bond character could be based on the bond length itself, a visual analysis of the σ and π molecular orbitals, or a quantitative analysis, for instance of the Morokuma-type,[8] of the contributions to bonding energy from a given choice of reference monomers. Here, we try to push the concept of triple bonds to its reasonable limits, but not beyond. A coherent bond length amplified by some $\sigma^2\pi^4$ character in the wave function will form an entrance ticket to the data set. Only a demonstrated, fully ionic character (or other proof of inappropriate behaviour) would lead to excommunication from it. To our knowledge, this is the first comprehensive set of triple-bond covalent radii proposed.

Results and Discussion

General remarks: Both theoretical and experimental data were used in the present fit. The primary data are given in Table 1. Omitted cases are given in Table 2.

The computational methods and the fitting approach are discussed in the Computational Details section at the end.

[a] Prof. P. Pyykkö, S. Riedel, M. Patzschke
Department of Chemistry, University of Helsinki
P.O.B. 55 (A.I. Virtasen aukio 1), 00014 Helsinki (Finland)
Fax: (+358) 9-191-40169
E-mail: Pekka.Pyykko@helsinki.fi
Sebastian.Riedel@mail.uni-wuerzburg.de

[b] S. Riedel
Institut für Anorganische Chemie, University of Würzburg
Am Hubland, 97074 Würzburg (Germany)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200401299

The converged radii are given in Figure 1, and the deviations from the predicted values are shown in Figure 2. We then discuss the various groups of the periodic table.

Group 1: No systems with a clear triple-bond character were found, not even for caesium. Therefore, the alkali metals were omitted from the present work, despite the fact that some evidence for 5d contributions to the bonding of Cs exists.[9] The molecules IrCs and $OsCs^+$ had short calculated bond lengths of 239.0 and 261.8 pm, respectively, but the bonds were mainly ionic. Parenthetically, a single-bond radius of 223 pm would result from Cs_2 ($R = 447$ pm[10]). Note also that the value of 253 pm in the VCH table[3] appears to be a perpetuated printing error.

Group 2: Barium is known to have substantial 5d character in its covalent bonds.[11,12] This was found to result in multiple bonding[9,13] to Ba if the ligands are capable of π bonding. In the present work, BaO, BaS and CsNBa were included but BaN^- was omitted. With respect to Be or Mg, the CO or SiO isoelectronic series can be continued to BeO^{2-}, BeF^- or MgO^{2-} ions. Although the present triple-bond radius values of 88 and 133 pm, for *r*(Be) and *r*(Mg), respectively, are not far below the single-bond values in the VCH periodic table (89 and 136 pm, respectively), they now coexist with the triple-bonded radii for their ligands (N, O, F, S). For molecules including Ca, Sr and Ra, see the tables. The predicted diatomic BaPt fits in perfectly and is a further example of the chemical analogy between platinum and oxygen.[14]

Group 3, lanthanides and actinides: The eight-electron (8e) systems ScN and YN have a well-developed $\sigma^2\pi^4$ multiple bond. The lanthanides were treated using available data for the 8e LaO^+ ion and the, effectively, 12e GdO^- and LuO^- ions. The homonuclear $\sigma^2\pi^4$ dimers La_2, Ce_2 and Pr_2 were included.[15] For the actinides, the database comprises the monoxide ThO, the f^0 actinyl series[16] and, notably, the triple bonds in the predicted N≡U≡Ir.[17] The Th–Th bond in the acetylene-like, predicted HThThH of Straka[18] was also included. It was shown by Marian et al.[19] that ThO has a clear $\sigma^2\pi^4$ bond. In the actinyls, like $O{\equiv}U{\equiv}O^{2+}$ and $\sigma_g^2\pi_g^4\sigma_u^2\pi_u^4$, the g orbitals bond to the metal 6d and the u orbitals to the metal 5f.[20,21] Hence, these bonds can also be called triple bonds.

Group 4: For Ti, TiC (Figure 3), $(Cp)_2TiO$ and TiO were used. $(Cp)_2MO$ and MO (M = Zr, Hf) provided data for the heavier congeners. RfC and RfO provided a value for Rf.

Group 5: The 10e systems VN, NbN (excited $S = 0$ state) and TaN (Figure 3) provided a systematic starting point. The TaO^+, X_3MO (M = V–Db, X = halogen) and η^4-L–VO systems were also used. Db was also included by means of the 8e DbB and DbC^+.

Group 6: Nitrides, such as $Cl_3W{-}N$ and $(MeO_3)W{-}N$, and oxides, $Cl_4Cr{-}O$, $Cl_4Mo{-}O$, Cl_2CrO_2 and $X_4W{-}O$, were used. Their heavier phosphide, arsenide, antimonide and bismuthide analogues $(MeO)_3M{-}E$, (M = Mo, W; E = P–Bi) were also used. Further primary data came from sulphides, $Cl_4M{-}S$ (M = Cr, Mo), $X_4W{-}S$ (X = F, Br), and selenides. Group-14 ligands $(Cp)(CO)_2Cr{-}Ge(aryl)$ and $Mo{-}GeR$ were included. For a Cr≡Cr triple bond, the present system would predict an *R* of 206 pm. No such unbridged examples seem to exist in the literature.[22] The existing unbridged compounds have the Cr atom in oxidation state (I) rather than (III).[23,24] They have a much longer *R* of 228 pm and 221.5 pm, respectively. The experimental data used for Mo≡Mo and W≡W bonds are shown in Table 1. Further comparable data exists in Tables 5.3.1. and 5.2.1. of Cotton and Walton.[22] These data are coherent with the heteronuclear M≡X radii. The considerably longer Mo–Mo bonds of 245 pm, found by Curtis,[25] and 249 pm, found by Dahl,[26] have "semibridging" carbonyls and are not clearly Mo^{III} compounds. For a general review of multiple bonds between metal atoms, see Cotton and Walton.[22]

Group 7: Various nitrides and oxides were used as primary data, as explained in Table 1. For a Re≡Re bond, the present radii predict an *R* of 220 pm, not far from the 229 pm in $[Re_2Cl_5(dth)_2]$ (dth = 1,5-dithiahexane).[27]

Group 8: Unlike Ru and Os, the 3d metal Fe no longer has reliable data for the highest oxidation state (VIII). In fact, it appears to be still unknown. For iron, very short effective radii would result from the experimentally unknown, excited singlet states of FeC and FeN^+; this *r*(Fe) would be 88 pm. Chemically more meaningful choices are the included diatomic FeO and a Fe≡Ga bond. For the high oxidation states of Ru and Os, the Cl_4MN^- nitrides (M = Ru, Os), the oxide Cl_4OsO, the 12e diatomic species RuC (Figure 3) and RuN^+, and the 14-valence-electron OsS were used. For an Os≡Os bond, the predicted *R* is 218 pm. A value of 219 pm occurs in the unbridged $[Os_2(CH_2CMe_3)_4(\eta^3\text{-}C_3H_5)_2]$.[28] For bridged complexes, longer values are observed.

Abstract in Finnish: *Alkuaineille Be–(E112) on määrätty $\sigma^2\pi^4$-kolmoissidoksille luonteenomaiset kovalenttiset säteet, rajatapaukset mukaan lukien. Vain ryhmän 1 alkuaineet, ryhmän 12 alkuaineet Zn–Hg, ryhmän 18 Ne sekä osa lantanoideista ja myöhemmät aktinoidit on tällöin kokonaan jätetty tarkastelun ulkopuolelle. Aineisto käsittää 324 pistettä ja tulosten standardipoikkeama on 3.2 pm.*

Abstract in German: *Ein System additiver kovalenter Radien für $\sigma^2\pi^4$ Dreifachbindungen fast aller Elemente von Be bis E112 (Eka-Quecksilber) wird vorgestellt. Grenzfälle mit schwachen Mehrfachbindungen wurden mit einbezogen. Die Elemente in Gruppe 1, Zn–Hg in Gruppe 12, Ne, die meisten Lantanide und einige Actinide wurden wegen mangelnder Daten nicht berücksichtigt. Die Standardabweichung für die 324 verwendeten Datenpunkte beträgt 3.2 pm.*

Table 1. The triple-bonded species used in the fit.

Z_1	Z_2	Distance	Species	Ref.	Z_1	Z_2	Distance	Species	Ref.	Z_1	Z_2	Distance	Species	Ref.
6	6	120.5	HCCH	[54]	6	73	184.9	$Ta(Cp^*)(CPh)(PMe_3)_2Cl$	[81]	7	79	181.2	AuN^{2+}	[94]
7	7	109.77	N_2	[10]	6	74	175.2	$Me_2ClW{-}CH$	[77]	7	83	193.489	BiN	[95]
8	8	105.7	O_2^{2+}	[55]	6	74	175.8	$Me_3W{-}CH$	[77]	7	85	191.5	$NAtO_3^{2-}$	pw
14	14	206.2	$R_3Si{-}SiSi{-}SiR_3$	[56]	6	74	172.07	WC	pw	7	86	186.6	$NRnO_3^-$	pw
14	14	207.2	$RSi{-}SiR$	[57]	6	74	173.1	Cl_3WCH	[82]	7	89	193.46	AcN	pw
14	14	207.2	$RSi{-}SiR$	[58]	6	77	165.08	IrC^-	pw	7	92	174	NUIr	[17]
15	15	189.34	P_2	[10]	6	78	167.67	PtC	[10]	7	105	175.66	DbN	pw
31	31	231.9	$Mes^*{}_2C_6H_3GaGa\text{-}C_6H_3Mes^*{}_2$	[59]	6	78	167.45	PtC	pw	7	107	172.74	Cl_4BhN	pw
33	33	210.26	As_2	[10]	6	79	181.0	AuC^+	pw	7	109	166.59	MtN	pw
42	42	216.7	$Mo_2(CH_2SiMe_3)_6$	[60]	6	104	192.89	RfC	pw	7	112	182.45	$(E112)N^{3+}$	pw
42	42	221.4	$Mo_2(NMe_2)_6$	[61]	6	105	188.57	DbC^+	pw	8	12	174.9	MgO	[10]
42	42	224	$Mo_2(Oc(CH_3)_3)_6$	[62]	6	106	179.06	SgC	pw	8	12	186.8	MgO^{2-}	[66]
51	51	248.78	Sb_2	[63]	6	109	173.22	MtC^-	pw	8	13	164.50	AlO^-	[68]
57	57	280	La_2	[15]	6	110	171.8	DsC	[42]	8	14	150.97	SiO	[10]
58	58	262	Ce_2	[15]	6	111	176.4	RgC^+	pw	8	15	145.5	Cl_3PO	[83]
59	59	255.5	Pr_2	[15]	6	112	190.84	$(E112)C^{2+}$	pw	8	15	143.7	F_3PO	[83]
74	74	225.5	$W_2(CH_2SiMe_3)_6$	[64]	7	8	106.32	NO^+	[10]	8	15	142.76	PO^+	[68]
74	74	229.2	$W_2(NMe_2)_6$	[65]	7	14	159.2	SiN^-	[68]	8	17	146.7	OCl^{3+}	[84]
74	74	230	$W_2Cl_4(NHCH_2CH_3)_2\text{-}(P(CH_3)_3)_2$	[62]	7	15	149.0866	PN	[10]	8	20	182.21	CaO	[10]
83	83	265.96	Bi_2	[10]	7	16	144.0	NS^+	[10]	8	22	159.97	TiO	[10]
90	90	271.1	HThThH	[18]	7	16	145.0	NSCl	[83]	8	22	161	$(Cp)_2TiO$	[96]
4	8	133.09	BeO	[10]	7	17	143.9	NCl^{2+}	[68]	8	22	161.3	(OEP)TiO	[97]
4	8	139.4	BeO^{2-}	[66]	7	17	146.6	O_3ClN^{2-}	[39]	8	23	162.0	(OEP)VO	[97]
4	9	142.5	BeF^-	[32]	7	18	146.2	O_3ArN^-	[39]	8	23	157.1	Cl_3VO	[98]
4	16	174.15	BeS	[10]	7	18	153.3	NAr^{3+}	[84]	8	23	158.2	Cl_3VO	[99]
4	16	184.3	BeS^{2-}	[66]	7	21	168.723	ScN	[85]	8	23	152.79	VO^+	pw
5	7	129.1	BN^{2-}	[32]	7	22	166	$N{-}TiN_3$	[86]	8	24	152	$[CrOX_4]^-$ X = Hal.	[90]
5	8	124.39	BO^-	[67]	7	23	154.6	VN	pw	8	24	157	$[CrO(O_2)(OH_2)]$	[62]
5	9	126.260	BF	[10]	7	24	154	$NCr(NiPr_2)_3$	[62]	8	24	155.7	Cl_4CrO	[99]
5	16	169.2	BS^-	[68]	7	25	151	MnN(TPP)	[87]	8	24	156.8	Cl_2CrO_2	[98]
5	17	171.59	BCl	[10]	7	27	150.37	CoN	pw	8	25	155.5	$[Et_4N][Mn(O\text{-}\eta^4\text{-}L)]$	[90]
5	21	185.95	ScB	pw[a]	7	28	157.66	NiN^+	pw	8	25	159	MnO_3F	[87]
5	29	192.27	CuB	pw	7	32	170.78	GeN^-	[88]	8	25	157.0	$ClMnO_3$	[98]
5	47	208.18	AgB	pw	7	33	161.843	AsN	[10]	8	26	159.35	FeO	pw
5	78	179.90	PtB^-	pw	7	35	163.4	$NBrO_3^{2-}$	pw	8	27	153.53	CoO^+	pw
5	79	192.27	AuB	pw	7	36	161.7	$NKrO_3^-$	pw	8	32	164.46	GeO	[10]
5	105	199.35	DbB	pw	7	39	178.9	YN	pw	8	33	156.8	AsO^+	[10]
5	111	191.69	RgB	pw	7	41	165.25	NbN	pw	8	38	191.983	SrO	[10]
6	7	117.7	CN^-	[69]	7	42	163.9	$[(MeO)_3Mo{-}N]$	[89]	8	39	174.63	YO^+	[100]
6	7	115.8	CH_3CN	[54]	7	42	165	$MoN(Mes)_3$	[62]	8	40	171.16	ZrO	[10]
6	8	112.83	CO	[10]	7	42	163.0	$MoNCl_4$	[62]	8	40	176	$(Cp)_2ZrO$	[96]
6	9	115.4255	CF^+	[70]	7	43	165	$NTcX_4$ X = Hal.	[90]	8	41	169.4	Br_3NbO	[101]
6	15	160.53	CP^-	[68]	7	43	155.9	$[TcNBr_4(OH_2)]^-$	[87]	8	41	171.1	Cl_3NbO	[98]
6	15	154.8	*t*Bu–CP	[71]	7	44	152.82	RuN^+	pw	8	41	164.62	NbO^+	pw
6	16	153.49	CS	[10]	7	44	157.0	$RuNCl_4^-$	[87]	8	42	165.8	Cl_4MoO	[102]
6	17	153.78	CCl^+	[72]	7	45	159.80	RhN	pw	8	42	169.7	Cl_4MoO	[99]
6	22	160.9	TiC	[73]	7	46	172.03	PdN^+	pw	8	42	164.6	$[MoO(NCS)_5]^{2-}$	[62]
6	27	152.07	CoC^-	pw	7	51	183.567	SbN	[91]	8	43	161.39	TcO^-	pw
6	28	162.73	NiC	[74]	7	53	183.8	NIO_3^{2-}	pw	8	43	163.18	TcO^-	pw
6	28	159.60	NiC	pw	7	54	180.2	$NXeO_3^-$	pw	8	43	170.7	$ClTcO_3$	[98]
6	29	180.69	CuC^+	pw	7	56	204.7	CsNBa	[13]	8	43	167.0	$TcOF_5$	[87]
6	33	165.7	Mes*–CAs	[75]	7	57	191.9	LaN	pw	8	43	163.2	$[Tc_2O_2F_9]^+$	[87]
6	34	167.65	CSe	[10]	7	71	183.5	LuN	pw	8	43	161.3	$[TcOBr_4]^-$	[87]
6	35	170.8	CBr^+	[76]	7	73	168.31	TaN	[92]	8	43	159.3	$[TcOCl_4]^-$	[87]
6	42	170.7	MoCH	[62]	7	73	168.31	TaN	pw	8	44	161.38	RuO	pw
6	42	174.0	$Me_3Mo{-}CH$	[77]	7	74	166.6	Cl_3WN	[93]	8	45	165.16	RhO^+	pw
6	42	173.6	$Me_2ClMo{-}CH$	[77]	7	74	167.0	$[(MeO)_3W{-}N]$	[89]	8	50	183.25	SnO	[10]
6	44	158.54	RuC	pw	7	75	165.67	Cl_4ReN	pw	8	53	171.5	F_5IO	[103]
6	44	160.79	RuC	[78,79]	7	75	158	Cl_4ReN	[87]	8	54	170.3	F_4XeO	[104]
6	45	161.52	RhC^-	pw	7	75	162	$[ReNX_4]^-$	[87]	8	56	193.97	BaO	[10]
6	46	169.8	PdC	[80]	7	76	160.4	Cl_4OsN^-	[87]	8	57	186.1	LaO^+	[105]
6	46	171.6	PdC	pw	7	77	159.06	IrN	pw	8	64	185	GdO^-	[106]
6	47	200.95	AgC^+	pw	7	78	163.18	PtN^+	pw	8	71	184	LuO^-	[106]

Table 1. (Continued)

Z_1	Z_2	Distance	Species	Ref.	Z_1	Z_2	Distance	Species	Ref.	Z_1	Z_2	Distance	Species	Ref.
8	72	172.31	HfO	[10]	14	79	222.2	$AuSi^+$	pw	31	79	245.26	AuGa	pw
8	72	176	$(Cp)_2HfO$	[96]	15	16	186.7	$HF_2P{-}S$	[83]	32	33	211.1	HGeAs	[120]
8	73	166.68	TaO^+	[10]	15	16	183.31	PS^+	pw	32	33	217.92	$GeAs^-$	pw
8	73	166.73	TaO^+	pw	15	27	189.82	CoP	pw	32	42	227.1	$(\eta^5\text{-Cp})(CO)_2Mo\text{-}GeC_6H_5\text{-}2,6\text{-}Mes_2$	[121]
8	73	176.5	Cl_3TaO	[99]	15	28	193.96	NiP^+	pw	32	42	227.2[b]	$(Cp)(CO)_2Mo{-}GeMe$	[117]
8	73	173.4	Cl_3TaO	[98]	15	32	210.68	GeP^-	[88]	32	42	231.4[c]	$[X(dppe)_2Mo{-}Ge(\eta^1\text{-}Cp^*)]$	[36]
8	74	166.6	F_4WO	[107]	15	33	199.9	AsP	[10]	32	74	227.7	$(\eta^5\text{-Cp})(CO)_2W\text{-}GeC_6H_3\text{-}2,6\text{-}Mes_2$	[117]
8	74	168.5	Cl_4WO	[107]	15	42	210.2	$[(MeO)_3Mo{-}P]$	[89]	32	74	230.2	$[Cl(dppe)_2W{-}Ge(\eta^1\text{-}Cp^*)]$	[35]
8	74	168.92	Cl_4WO	pw	15	42	211	$MoP(NiPrAr)_3$	[62]	33	34	208.05	$AsSe^+$	pw
8	74	168.4	Br_4WO	[107]	15	45	198.24	RhP	pw	33	42	225.2	$MoAs(N_3N)$	[62]
8	75	164.57	ReO^-	pw	15	51	220.544	SbP	[91]	33	42	222.4	$[(MeO)_3Mo{-}As]$	[89]
8	75	165.30	ReO^-	pw	15	74	212.7	$[(RO)_3WPM(CO)_5]$	[113]	33	74	224.5	$[(MeO)_3W{-}As]$	[89]
8	75	164.2	F_5ReO	[108]	15	74	212.6	$[(MeO)_3W{-}P]$	[89]	33	83	239.075	BiAs	[122]
8	75	163	$[ReOCl_4](H_2O)$	[87]	15	77	197.96	IrP	pw	34	49	247.65	$InSe^-$	pw
8	76	166.3	Cl_4OsO	[102]	15	83	229.615	BiP	[95]	34	73	230.6	Cl_3TaSe	[99]
8	76	166.82	Cl_4OsO	pw	16	20	231.78	CaS	[10]	34	74	226.0	Cl_4WSe	[99]
8	76	160.18	OsO	pw	16	23	206.1	VS(acen)	[114]	34	74	222.6	F_4WSe	[107]
8	77	161.48	IrO^+	pw	16	23	202.6	Cl_3VS	[99]	34	74	220.3	Cl_4WSe	[107]
8	82	192.18	PbO	[10]	16	24	198.7	Cl_4CrS	[99]	34	74	222.0	Br_4WSe	[107]
8	88	211.33	RaO	pw	16	26	192.67	FeS	pw	34	81	255.31	$TlSe^-$	pw
8	90	184.03	ThO	[10]	16	31	213.3	GaS^-	[115]	34	82	240.22	PbSe	[95]
8	91	181.2	$OPaO^+$	[16]	16	33	194.47	AsS^+	[10]	42	51	243.6	$[(MeO)_3Mo{-}Sb]$	[89]
8	92	171.5	OUO^{2+}	[109]	16	40	216.6676	ZrS	[116]	42	83	248.8	$[(MeO)_3Mo{-}Bi]$	[89]
8	93	168.2	NpO_2^{3+}	[16]	16	41	210.4	av of $X_3(SPPH_3)Nb{-}S$ and $X_4Nb{-}S^-$	[114]	49	77	257.1	$[(NC)_5Ir{-}In(CN)]^{2-}$	pw
8	104	180.97	RfO	pw	16	41	212.0	Cl_3NbS	[101]	49	78	256.2	$[(dcpe)Pt(InCp^*)_2]$	[119]
8	105	178.98	Cl_3DbO	pw	16	41	213.4	Br_3NbS	[101]	49	78	256.7	$[(NC)_5Ir{-}In(CN)]^-$	pw
8	106	176.08	Cl_4SgO	pw	16	42	211.3	Cl_4MoS	[99]	50	51	258.5	$SnSb^-$	pw
8	107	172.22	BhO^-	pw	16	44	199.57	RuS	pw	50	52	252.3	SnTe	[10]
8	108	173.52	Cl_4HsO	pw	16	56	250.74	BaS	[10]	50	74	249.0	$[Cl(Me_3P)_4W{-}Sn(C_6H_3\text{-}2,6\text{-}Mes_2)]$	[37]
9	13	165.44	AlF	[10]	16	73	218.5	Cl_3TaS	[99]	50	74	250.4	$[Cl(dppe)_2W{-}SnR]$	[123]
9	14	153.1	SiF^+	[84]	16	74	214.2	Cl_4WS	[99]	50	74	246.4	$[(dppe)_2W{-}Sn(C_6H_3\text{-}2,6\text{-}Mes_2)]^+$	[123]
9	15	144.30	PF^{2+}	[68]	16	74	210.4	F_4WS	[107]	51	52	246.6	$SbTe^+$	pw
9	16	145.7	SF^{3+}	[84]	16	74	208.6	Cl_4WS	[107]	51	74	245.5	$[(MeO)_3W{-}Sb]$	[89]
12	16	214.25	MgS	[10]	16	74	210.9	Br_4WS	[107]	52	82	259.49	PbTe	[10, 95]
12	16	226.9	MgS^{2-}	[66]	16	76	198.43	OsS	pw	56	78	257.3	BaPt	pw
13	16	209.3	AlS^-	[110]	16	82	228.68	PbS	[10]	74	82	254.77	$[I(Me_3P)_4W{-}Pb(C_6H_3\text{-}2,6\text{-}Trip_2)]$	[38]
13	17	199.4	$AlCl^{2+}$	[111]	23	34	214.8	Cl_3VSe	[99]	74	83	250.8	$[(MeO)_3W{-}Bi]$	[89]
13	79	233.84	AuAl	[10]	24	32	216.7	$(Cp)(CO)_2Cr{-}GeMe$	[117]	77	92	218.4	NUIr	[17]
14	15	201.45	SiP^-	pw	24	32	216.66	$(Cp)(CO)_2Cr{-}Ge(aryl)$	[118]	77	81	257.2	$[(NC)_5Ir{-}Tl(CN)]^{2-}$	pw
14	28	200.36	NiSi	pw	24	34	211.2	Cl_4CrSe	[99]	78	81	259.6	$[(NC)_5Pt{-}Tl(CN)]^-$	pw
14	33	213.5	$SiAs^-$	[88]	26	31	222.5	$(CO)_4Fe{-}GaR$	[59]	78	90	250	PtTh	[124]
14	46	210.91	PdSi	pw	31	34	228.6	$GaSe^-$	pw	82	83	271.25	$PbBi^-$	pw
14	47	238.10	$AgSi^+$	pw	31	77	234.6	$[(NC)_5Ir{-}Ga(CN)]^{2-}$	pw	83	84	263.2	$BiPo^+$	pw
14	78	206.29	PtSi	[112]	31	78	231.6	$[(dcpe)Pt(GaC(SiMe_3)_3]_2$	[119]					
14	78	208.22	PtSi	pw	31	78	238.6	$[(NC)_5Pt{-}Ga(CN)]^-$	pw					

[a] pw = present work. [b] Mean value of two different X-ray experiments. [c] Mean value for X = Cl and Br.

Group 9: Here the 14 e diatomic systems CoC^-, RhC^-, IrC^- and MtC^- or CoN, RhN, IrN and MtN provided a systematic data set. For the valence isoelectronic molecule RhP, an experimental R of 186 pm was claimed by Li and Balfour.[29] Our calculated value is 198.2 pm. The present sum of our triple-bond radii would give 200.5 pm. Thus the experimental RuP bond length remains unconfirmed.

Group 10: The closed-shell molecules NiC, PdC, PtC (Figure 3) and DsC provide a systematic starting point. The isoelectronic PtB^- ion was included to augment the data.

Group 11: In the coinage-metal group (M = Cu, Ag, Au, Rg; Rg = roentgenium, E 111), the AuC^+ ion was identified as a potential triple bond[30] before its experimental detec-

Table 2. List of outlier data points, which are not included in the fit.

Z_1	Z_2	Distance	Species	Reference	Reason[a]
6	26	147.83	FeC(S=0)	pw	a
7	26	142.22	FeN^+	pw	a
8	16	138.06	SO^{2+}	[68]	a
16	16	178.9	S_2^{2+}	[125]	a
8	44	170.5	RuO_4	[54]	b
8	76	171	OsO_4	[54]	b
8	42	170.5	Cl_2MoO_2	[98]	b
8	74	173.1	Cl_2WO_2	[98]	b
8	75	174.2	$ClReO_3$	[98]	b
49	79	266.8	AuIn	pw	c
79	81	276.3	AuTl	pw	c
6	76	168.82	OsC	pw	d
7	76	162.61	OsN^+	pw	d
5	26	168.96	FeB^-	pw	d
5	44	178.62	RuB^-	pw	d
5	76	181.76	OsB^-	pw	d
7	27	157.5	CoN		d
6	33	173.5	CAs^-	[88]	d
24	24	191	Cr_2H_6	[126]	e
24	24	195	Cr_2H_6	[127]	e
8	26	158.1	FeO_4	[98]	b, f
16	40	228	$(Cp)_2ZrS$	[96]	g
16	72	228	$(Cp)_2HfS$	[96]	g
34	40	242	$(Cp)_2ZrSe$	[96]	g
34	72	241	$(Cp)_2HfSe$	[96]	g

[a] Reason a: Too small; b: more than one oxygen atom; c: not actually triple bonds; d: not coherent with included systems δ^2; e: omit the badly defined, experimentally unknown Cr–Cr case; f: omit the tetracoordinate, unknown Fe^{VIII} species; g: too long $(Cp)_2M–E$ bond.

tion.[31] The valence isoelectronic molecules MB (M = Cu–Rg) are included, of which Cu and Ag are limiting cases, showing only traces of π bonding. Note that Rg has the smallest triple-bond radius in Group 11, which can be attributed to relativistic effects. The heavier analogues AuAl and AuGa were included, whereas AuIn and AuTl showed no triple-bond character upon visual inspection, and were omitted.

Group 12: For eka-mercury (E112), the previous diatomic isoelectronic series could be continued to $(E112)C^{2+}$. For elements Zn–Hg there are no data.

Group 13: For boron, BF and its valence isoelectronic neighbours have enough multiple-bonding character[32,33] to be included. Several valence isoelectronic diatomic systems for Al–Tl were also included. A different cross-check for the present radii are the Ir–Ga, Pt–Ga, Ir–In, Pt–In, Ir–Tl and Pt–Tl bonds. With respect to the Ga≡Ga triple bond suggested by Robinson's group,[34] our results do not disagree with the idea. In fact, their homonuclear Ga–Ga bond length of 232 pm is shorter than twice the present r(Ga) value of 121 pm, largely based on heteronuclear pairs.

Group 14: Acetylene and its silicon analogues are fundamental examples of triple bonds. As mentioned, the series CO–CSe, SiO–PbO and SiS–PbS, as well as the isoelectronic SnTe and PbTe molecules and certain ions are included in the data set. Note the recent triple bonds from Ge, Sn and Pb to Group-6 elements[35–38] in Table 1.

Group 15: The series N_2 to Bi_2, including many heteronuclear dimers, was the starting point of the present study. Note the HCN and CN^- analogues HGeAs and $GeAs^-$, up to $PbBi^-$. Many nitrides and some phosphides, arsenides, antimonides and bismuthides of transition metals are included in the data set. As a high-valent case, note Cl_3P^VO.

Group 16: Oxides to tellurides were already quoted. Po occurs in the $BiPo^+$ ion. As a ligand, Te is often on the long side and many such cases were omitted.

Group 17: For fluorine, we have BF and CF^+. For Cl, NCl^{2+}, OCl^{3+} and $AlCl^{2+}$ (8e) ions and the $Cl^{VII}N$ bond of the O_3ClN^{2-} ion were used. For the heavier halogens, $O_3X{\equiv}N^{2-}$ species (X = Cl, Br, I, At) were included.

Group 18: For Ne, no example can be found. For Ar, the $O_3Ar{\equiv}N^-$, predicted by Pyykkö,[39] and NAr^{3+} species were included. The pentaatomic series $O_3Ng{\equiv}N^-$ is now extended to Ng = Kr, Xe and Rn.

Periodic trends: For the transition metals of Groups 4–9, a general trend is $3d \ll 4d \leq 5d$. Note that for Fe, smaller oxidation states were used than for the heavier analogues Ru and Os. At Groups 10–12, the "gold maximum" of relativistic effects changes the trend: Pt is smaller

	1												13	14	15	16	17	18
1	H -	2																He -
2	Li -	Be 85											B 73	C 60	N 54	O 53	F 53	Ne -
3	Na -	Mg 127	3	4	5	6	7	8	9	10	11	12	Al 111	Si 102	P 94	S 95	Cl 93	Ar 96
4	K -	Ca 133	Sc 114	Ti 108	V 106	Cr 103	Mn 103	Fe 102	Co 96	Ni 101	Cu 120	Zn -	Ga 121	Ge 114	As 106	Se 107	Br 110	Kr 108
5	Rb -	Sr 139	Y 124	Zr 121	Nb 116	Mo 113	Tc 110	Ru 103	Rh 106	Pd 112	Ag 137	Cd -	In 146	Sn 132	Sb 127	Te 121	I 125	Xe 122
6	Cs -	Ba 149	La 139	Hf 122	Ta 119	W 115	Re 110	Os 109	Ir 107	Pt 110	Au 123	Hg -	Tl 150	Pb 137	Bi 135	Po 129	At 138	Rn 133
7	Fr -	Ra 159	Ac 140	Rf 131	Db 126	Sg 121	Bh 119	Hs 118	Mt 113	Ds 112	Rg 118	E112 130						

6	Ce 131	Pr 128	Nd -	Pm -	Sm -	Eu -	Gd 132	Tb -	Dy -	Ho -	Er -	Tm -	Yb -	Lu 131
7	Th 136	Pa 129	U 118	Np 116	Pu -	Am -	Cm -	Bk -	Cf -	Es -	Fm -	Md -	No -	Lr -

Figure 1. The proposed triple-bond covalent radii in pm.

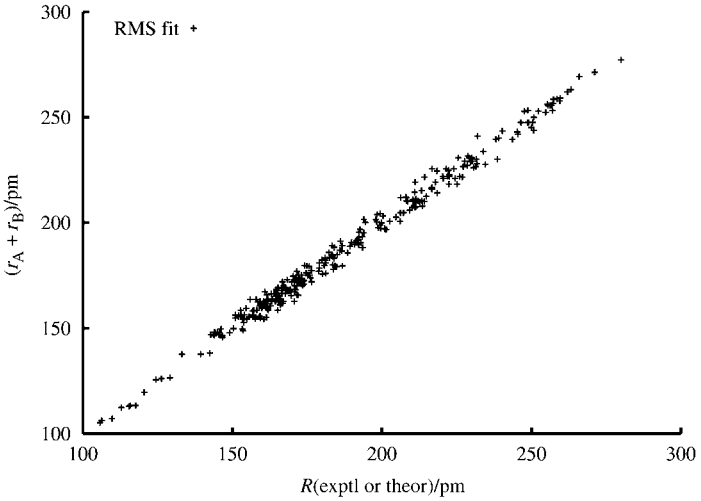

Figure 2. The correlation between predicted and observed bond length for the data in Table 1.

than Pd, and Au is far smaller than Ag. Rg is still smaller. E112 is the only Group-12 element that could be included here.

Along a long row, a broad minimum would seem to occur near Groups 8 to 9, with a reservation for the changes of oxidation state. Among the p elements, a monotonous decrease of r would seem to take place from Group 13 to, or almost to, Group 18.

As a function of the row, the main-group elements show the trend $2p \ll 3p < 4p < 5p \leq 6p$. Note here the anomalously small size of the nodeless 2p shell.[40,41]

Along the actinide row, the effective triple-bond radii decrease from Ac to Np.

The 6d elements in Groups 4–9 are about 6–10 pm larger than their 5d analogues. From Group 10 to 12, near the "gold maximum" of relativistic effects in Group 11, the 6d elements develop remarkably short bonds. RgB and RgC^+ are the smallest members in Group 11, even smaller than CuB and CuC^+, respectively. Up to Groups 9 or 10, the transactinides still form another normal d series. In Groups 11 and 12, a transactinide break[42] becomes apparent (Figure 4).

Conclusions

We present a self-consistent set of operational additive covalent radii for 81 elements on the basis of 324 experimental and theoretical data points. These radii have a potential predictive value when assessing 81 homonuclear or 3240 heteronuclear triple bonds, most of them still unknown. Further data can also be used to either improve or partially invalidate the present system of radii.

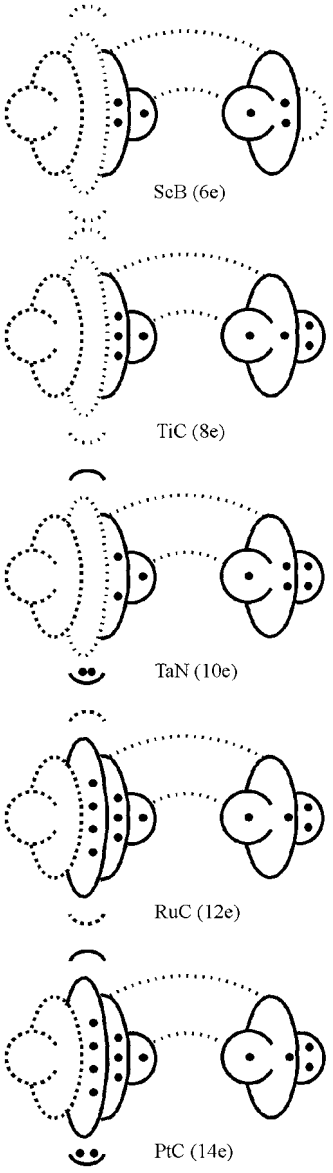

Figure 3. Cartoon of diatomic species with different numbers of electrons.

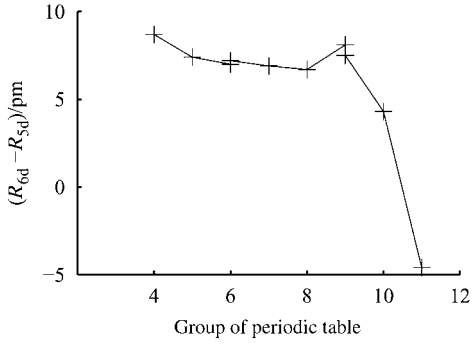

Figure 4. The difference in the lengths of the triple bonds between 6d and 5d metals for the cases in Table 1. Note the transactinide break taking place in Groups 10 and 11.

Computational Details

Data and fitting methods: Both experimental and computed bond lengths were used. The experimental data comprised both gas-phase molecular data and crystal-structure data. No attempt was made to even out the "noise", corresponding to the standard deviation.

A first fit was made manually, starting from the Group-15 homonuclear diatomic species N_2 to Bi_2. The heteronuclear diatomics also fitted well. The diatomic species CO to PbO provided preliminary radii for oxygen and its heavier homologues in Group 16. Acetylene gave the traditional r(C). All this opened the route to metal radii using the carbides, acetylides, nitrides or oxides. A more detailed discussion of the chemical systems was given above.

Using these starting values, an iterative program was written based on the penalty function over homonuclear and heteronuclear pairs [Equation (2)].

$$\sum_k (\Delta_k)^2 = \sum_i^{K_{\text{homo}}} (R_{ii}-2r_i)^2 + \sum_{ij}^{K_{\text{hetero}}} (R_{ij}-r_i-r_j)^2 \qquad (2)$$

Putting its derivatives with respect to r_i equal to zero, one obtains the iterative algorithm given in Equation (3).

$$r_i^{(N+1)} = \frac{1}{4K_{\text{homo}} + K_{\text{hetero}}} \left[\sum_i^{K_{\text{homo}}} 2R_{ii} + \sum_j^{K_{\text{hetero}}} (R_{ij}-r_j^{(N)}) \right] \qquad (3)$$

Here K is the number of data points in each set and N the iteration. No convergence difficulties or signs of multiple minima were noticed. The final data set had 324 points, used for fitting 81 radii. The standard deviation (given by Equation (4)) was 3.2 pm.

$$\varepsilon = \left[(\sum_{\text{tot}}^{K} \Delta^2)/K_{\text{tot}} \right]^{1/2}, \quad K_{\text{tot}} = K_{\text{homo}} + K_{\text{hetero}} \qquad (4)$$

Quantum chemical methods: The calibration of the methods and basis sets for our own calculations are shown in Table S1 of the Supporting Information. All calculated bond distances on every validated level and basis set are in good agreement with the experimentally known bond distances. It is seen from the results that the validated methods give values that are close to the experimental ones, but no obvious trends could be identified. The largest calculated error for the validated molecules was smaller than 4%. Due to this result we decided to use the TZVPP basis set for the main-group elements B–Se. For the heavier main-group elements we used the relativistic large core (RLC) ECP and the corresponding basis set from the Stuttgart group.[43] All transition metals were described by using the relativistic small core (RSC) ECP and the corresponding basis set from the Stuttgart group[43] (see also below). The halogen and rare gas species NXO_3^{n-} were described by the cc-pVTZ basis set. The well-known density functional B3LYP[44] was used for our production work.

The calculations on transactinide compounds were exceptions. Here a TZV2P basis set was used with the PW91-PW91[45] density functional. These calculations were carried out with a different code (see below for details).

Further exceptions were the X≡N and *Ng*≡N bonds in O_3XN^{2-} and O_3NgN^- (X = Cl–At, *Ng* = Ar–Rn). All of these bonds were treated at MP2 level, and for At and Rn, aug-cc-pVTZ-PP basis sets were used.

Calibration: In particular, to get comparable data for all elements in a column of the periodic system, ab initio and density functional calculations were performed using quantum chemical program packages Gaussian 03[44] and ADF[46] (for the transactinides). To establish a reasonably accurate and efficient computational methodology, we at first performed a calibration using some experimentally known systems, such as IrN, PtC, PtSi, CuAl, AgAl and AuAl. We compared the following density functionals: local density approximation in the form of the SVWN5[47] functional, the gradient-corrected BP86[48,49] functional, and the hybrid functionals B3LYP[44] (based on the work of Becke[50]) and BHandHLYP.[51] In addition, ab initio MP2, CCSD and CCSD(T) calculations were done for the calibration study. Three different basis-set combinations were compared, denoted by a, b and c (see Table S2 in Supporting Information). The scalar relativistic effects for the transition metals were included by using the quasirelativistic, small-core pseudopotentials (effective-core potential, ECP) of the Stuttgart group.[43] The corresponding basis sets of the transition metals were augmented by one polarization f-function (see ref. [52]). For the main-group elements, we used various basis sets: a) dunn-DZP, b) aug-cc-pVTZ and c) Ahlrichs TZV basis set augmented with polarization functions of the cc-pVTZ (i.e., two d-functions and one f-function) yielding the so called TZVPP basis set. Based on the calibration study (see above), the density functional B3LYP was used with the following basis set combinations: basis set c for the lighter elements, and an enlarged basis set together with ECPs for the heavier elements (see Table S1). The structures were optimized with standard gradient methods available in Gaussian 03.[44] The lowest singlet and triplet states were calculated for each considered molecule.

To treat all transactinides with the same accuracy, we chose ADF to do the calculations, the reason being that similar frozen cores and basis sets are available in this program for all the transactinides considered. Relativistic effects were treated with the zeroth-order regular approximation (ZORA)[53] method. The innermost electrons of the heavy metals were treated as frozen, using small frozen cores. For all elements, TZV2P basis sets were used. It should be noted that ADF employs Slater-type basis functions instead of Gaussian-type functions. No hybrid functionals are available in ADF. Therefore, we chose the PW91-PW91[45] functional. All transactinide compounds were checked for triplet-instabilities by calculating the excitation energies for the lowest triplet states.

Note on diatomics: To obtain a systematic sequence of data, many of the calculated systems were diatomics, having 6 to 14 valence electrons. The systems with 14 valence electrons could be described by a cartoon,[42] in which, in addition to the six electrons in the $\sigma^2\pi^4$ system, there is room for four electrons in a "delta ring", δ^4, two electrons in σ lone pairs at each end and two electrons in one σ "doughnut" pair on the metal atom. If the system prefers a δ^2 configuration with a half-filled δ ring, the two electrons go to a further σ orbital and lengthen the bond. Such systems were removed from the data set.

Acknowledgements

This work was supported by The Academy of Finland, projects 200903 and 206102, and by the Magnus Ehrnrooth Foundation. We are grateful to Michal Straka and the group of Prof. Martin Kaupp for their technical assistance.

[1] L. Pauling, *The Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithaca, NY, **1945**.
[2] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.
[3] E. Fluck, K. G. Heumann, Periodensystem der Elemente, 3. Auflage, Wiley-VCH, Weinheim, **2002**.
[4] W. L. Bragg, *Philos. Mag.* **1920**, *40*, 169–189.
[5] J. A. Wasastjerna, *Comm. Phys.-Math. Soc. Sci. Fennica* **1923**, *1*, No. 38, 1–25.
[6] R. D. Shannon, C. T. Prewitt, *Acta Crystallogr.* **1969**, *B25*, 925–946.
[7] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751–767.
[8] K. Morokuma, *J. Chem. Phys.* **1971**, *55*, 1236–1244.
[9] L. Gagliardi, P. Pyykkö, *Theor. Chem. Acc.* **2003**, *110*, 205–210.
[10] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand, New York, **1979**.
[11] P. Pyykkö, *J. Chem. Soc. Faraday Trans. 2* **1979**, *75*, 1256–1276.

[12] P. Pyykkö, J. G. Snijders, E. J. Baerends, *Chem. Phys. Lett.* **1981**, *83*, 432–437.
[13] L. Gagliardi, *J. Am. Chem. Soc.* **2002**, *124*, 8757–8761.
[14] P. Pyykkö, M. Patzschke, J. Suurpere, *Chem. Phys. Lett.* **2003**, *381*, 45–52.
[15] X.-Y. Cao, M. Dolg, *Mol. Phys.* **2003**, *101*, 1967–1976.
[16] M. Straka, K. G. Dyall, P. Pyykkö, *Theor. Chem. Acc.* **2001**, *106*, 393–403.
[17] L. Gagliardi, P. Pyykkö, *Angew. Chem.* **2004**, *116*, 1599–1602; *Angew. Chem. Int. Ed.* **2004**, *43*, 1573–1576.
[18] M. Straka, as quoted in ref. [17].
[19] C. M. Marian, U. Wahlgren, O. Gropen, P. Pyykkö, *J. Mol. Struct.: THEOCHEM* **1988**, *169*, 339–354.
[20] R. G. Denning, *Struct. Bonding (Berlin)* **1992**, *79*, 215–276.
[21] P. Pyykkö, J. Li, N. Runeberg, *J. Phys. Chem.* **1994**, *98*, 4809–4813.
[22] F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Clarendon Press, Oxford, **1993**.
[23] J. Potenza, P. Giordano, D. Mastropaolo, A. Efraty, R. B. King, *J. Chem. Soc. Chem. Commun.* **1972**, 1333–1334.
[24] M. D. Curtis, W. B. Butler, *J. Organomet. Chem.* **1978**, *155*, 131–145.
[25] R. J. Klingler, W. M. Butler, M. D. Curtis, *J. Am. Chem. Soc.* **1978**, *100*, 5034–5039.
[26] J.-S. Huang, L. F. Dahl, *J. Organomet. Chem.* **1983**, *243*, 57–68.
[27] M. J. Bennett, F. A. Cotton, R. A. Walton, *Proc. R. Soc. London Ser. A* **1968**, *303*, 175–192.
[28] R. P. Tooze, M. Motevalli, M. B. Hursthouse, G. Wilkinson, *J. Chem. Soc. Chem. Commun.* **1984**, 799–800.
[29] R.-H. Li, W. J. Balfour, *J. Phys. Chem. A* **2004**, *108*, 8145–8146.
[30] M. Barysz, P. Pyykkö, *Chem. Phys. Lett.* **1998**, *285*, 398–403.
[31] F. Aguirre, J. Husband, C. J. Thompson, R. B. Metz, *Chem. Phys. Lett.* **2000**, *318*, 466–470.
[32] P. Pyykkö, *Mol. Phys.* **1989**, *67*, 871–878.
[33] C. Esterhuysen, G. Frenking, *Theor. Chem. Acc.* **2004**, *111*, 381–389.
[34] J.-R. Su, X.-W. Li, C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471–5472.
[35] A. C. Filippou, A. I. Philippopoulos, P. Portius, D. U. Neumann, *Angew. Chem.* **2000**, *112*, 2881–2884; *Angew. Chem. Int. Ed.* **2000**, *39*, 2778–2781.
[36] A. C. Filippou, P. P. Portius, A. I. Philippopoulos, *Organometallics* **2002**, *21*, 653–661.
[37] A. C. Filippou, P. Portius, A. I. Philippopoulos, H. Rohde, *Angew. Chem.* **2003**, *115*, 461–464; *Angew. Chem. Int. Ed.* **2003**, *42*, 445–447.
[38] A. C. Filippou, N. Weidemann, G. Schnakenburg, H. Rohde, A. I. Philippopoulos, *Angew. Chem.* **2004**, *116*, 6674–6678; *Angew. Chem. Int. Ed.* **2004**, *43*, 6512–6516.
[39] P. Pyykkö, *Chem. Eur. J.* **2000**, *6*, 2145–2151.
[40] P. Pyykkö, *J. Chem. Res. Synop.* **1979**, 380–381.
[41] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262–286; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272–295.
[42] M. Patzschke, P. Pyykkö, *Chem. Commun.* **2004**, 1982–1983.
[43] http://www.theochem.uni-stuttgart.de/pseudopotentials/index.en.html.
[44] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[45] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671–6687.
[46] ADF2004.01 (http://www.scm.com), E. J. Baerends, J. A. Autschbach, A. Bérces, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, L. Fan, T. H. Fischer, C. Fonseca Guerra, S. J. A. van Gisbergen, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, F. E. Harris, P. van den Hoek, H. Jacobsen, G. van Kessel, F. Kootstra, E. van Lenthe, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. G. Snijders, M. Sola, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, O. Visser, E. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, and T. Ziegler, Theoretical Chemistry, Vrije Universiteit, Amsterdam, **2004**.
[47] S. J. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.
[48] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
[49] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.
[50] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[51] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
[52] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111–114.
[53] S. Faas, J. H. van Lenthe, A. C. Hennum, J. G. Snijders, *J. Chem. Phys.* **2000**, *113*, 4052–4059.
[54] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, **1984**.
[55] R. H. Nobes, D. Moncrieff, M. W. Wong, L. Radom, P. M. W. Gill, J. A. Pople, *Chem. Phys. Lett.* **1991**, *182*, 216–224.
[56] A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science* **2004**, *305*, 1755–1757.
[57] N. Takagi, S. Nagase, *Eur. J. Inorg. Chem.* **2002**, 2775–2778.
[58] N. Wiberg, S. K. Vasisht, G. Fischer, P. Mayer, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823–1828.
[59] J. Su, X.-W. Li, R. C. Crittendon, C. F. Campana, G. H. Robinson, *Organometallics* **1997**, *16*, 4511–4513.
[60] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, G. Wilkinson, *J. Chem. Soc. D. Chem. Commun.* **1971**, 1079–1080.
[61] M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, B. R. Stults, *J. Am. Chem. Soc.* **1976**, *98*, 4469–4476.
[62] A. G. Wedd in *Comprehensive Coordination Chemistry II, Vol. 4*, Elsevier, Oxford, **2004**.
[63] M. L. Polak, G. Gerber, J. Ho, W. C. Lineberger, *J. Chem. Phys.* **1992**, *97*, 8990–9000.
[64] M. H. Chisholm, F. A. Cotton, M. Extine, B. R. Stults, *Inorg. Chem.* **1976**, *15*, 2252–2257.
[65] M. H. Chisholm, F. A. Cotton, M. Extine, B. R. Stults, *J. Am. Chem. Soc.* **1976**, *98*, 4477–4485.
[66] A. I. Boldyrev, J. Simons, *J. Chem. Phys.* **1993**, *98*, 4745–4752.
[67] K. A. Peterson, R. C. Woods, *J. Chem. Phys.* **1989**, *90*, 7239–7250.
[68] K. A. Peterson, R. C. Woods, *J. Chem. Phys.* **1991**, *95*, 3528–3535.
[69] S. E. Bradforth, E. H. Kim, D. W. Arnold, D. M. Neumark, *J. Chem. Phys.* **1993**, *98*, 800–810.
[70] G. M. Plummer, T. Anderson, E. Herbst, F. C. D. Lucia, *J. Chem. Phys.* **1986**, *84*, 2427–2428.
[71] M. Finze, E. Bernhard, H. Willner, C. W. Lehmann, *Angew. Chem.* **2004**, *116*, 4254–4257; *Angew. Chem. Int. Ed.* **2004**, *43*, 4160–4163.
[72] Y. Pak, R. C. Woods, *J. Chem. Phys.* **1997**, *107*, 5094–5102.
[73] G. L. Gutsev, C. W. Bauschlicher, Jr., *J. Phys. Chem. A* **2003**, *107*, 4755–4767.
[74] D. J. Brugh, M. D. Morse, *J. Chem. Phys.* **2002**, *117*, 10703–10714.
[75] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3503, see p. 3495.
[76] Z. Li, *J. Chem. Phys.* **1998**, *109*, 134–138.
[77] S.-H. Choi, Z.-Y. Lin, Z.-L. Xue, *Organometallics* **1999**, *18*, 5488–5495.
[78] J. D. Langenberg, R. S. DaBell, L. D. Dreessen, M. D. Morse, *J. Chem. Phys.* **1998**, *109*, 7863–7875.

[79] T. C. Steimle, W. Virgo, *J. Chem. Phys.* **2003**, *119*, 12965–12972.
[80] I. Shim, K. A. Gingerich, *ChemPhysChem* **2001**, *2*, 125–130.
[81] S. J. McLain, C. D. Wood, L. W. Messerie, R. R. Schrock, F. J. Hollander, W. J. Youngs, M. R. Churchill, *J. Am. Chem. Soc.* **1978**, *100*, 5962–5964.
[82] S. F. Vyboishchikov, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 1439–1448.
[83] M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, A. G. Maki, *J. Phys. Chem. Ref. Data* **1979**, *8*, 619–721.
[84] M. W. Wong, L. Radom, *J. Phys. Chem.* **1990**, *94*, 638–644.
[85] R. S. Ram, P. F. Bernath, *J. Chem. Phys.* **1992**, *96*, 6344–6347.
[86] L. Gagliardi, P. Pyykkö, *Inorg. Chem.* **2003**, *42*, 3074–3078.
[87] E. C. Constable, J. R. Dilworth in *Comprehensive Coordination Chemistry II, Vol. 5*, Elsevier, Oxford, **2004**.
[88] J. Kalcher, *Phys. Chem. Chem. Phys.* **2002**, *4*, 3311–3317.
[89] K. K. Pandey, G. Frenking, *Eur. J. Inorg. Chem.* **2004**, 4388–4395.
[90] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, **1999**.
[91] S. A. Cooke, M. C. L. Gerry, *Phys. Chem. Chem. Phys.* **2004**, *6*, 4579–4585.
[92] R. S. Ram, J. Lievin, P. F. Bernath, *J. Mol. Spectrosc.* **2002**, *215*, 275–284.
[93] P. Spuhler, M. Lein, G. Frenking, *Z. Anorg. Allg. Chem.* **2003**, *629*, 803–815.
[94] P. Pyykkö, F. Mendizabal, *Inorg. Chem.* **1998**, *37*, 3018–3025.
[95] S. A. Cooke, J. M. Michaud, M. C. L. Gerry, *J. Mol. Struct.* **2004**, *695–696*, 13–22.
[96] M. T. Benson, T. R. Cundari, S. J. Lim, H. D. Nguyen, K. Pierce-Beaver, *J. Am. Chem. Soc.* **1994**, *116*, 3955–3966.
[97] R. Guilard, C. Lecomte, *Coord. Chem. Rev.* **1985**, *65*, 87–113.
[98] L. Deng, T. Ziegler, *Organometallics* **1996**, *15*, 3011–3021.
[99] O. González-Blanco, V. Branchadell, K. Monteyne, T. Ziegler, *Inorg. Chem.* **1998**, *37*, 1744–1748.
[100] C. Linton, B. Simard, H. P. Loock, S. Wallin, G. K. Rothschopf, R. F. Gunion, M. D. Morse, P. B. Armentrout, *J. Chem. Phys.* **1999**, *111*, 5017–5026.
[101] I. Nowak, E. M. Page, D. A. Rice, A. D. Richardson, R. J. French, K. Hedberg, J. S. Ogden, *Inorg. Chem.* **2003**, *42*, 1296–1305.
[102] A. Neuhaus, A. Veldkamp, G. Frenking, *Inorg. Chem.* **1994**, *33*, 5278–5286.
[103] K. S. Krasnov, *Molecular Constants of Inorganic Compounds (in Russian)*, Khimiya, Leningrad, **1979**.
[104] A. F. Hollemann, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 4th ed., Walter de Gruyter, Berlin, **1995**.
[105] D. Schröder, H. Schwarz, J. N. Harvey, *J. Phys. Chem. A* **2000**, *104*, 11257–11260.
[106] S. P. Willson, L. Andrews, *J. Phys. Chem. A* **1999**, *103*, 6972–6983.
[107] E. M. Page, D. A. Rice, K. Hagen, L. Hedberg, K. Hedberg, *Inorg. Chem.* **1991**, *30*, 4758–4761.
[108] T. R. Cundari, R. R. Conry, E. Spaltenstein, S. C. Critchlow, K. A. Hall, S. K. Tahmassebi, J. M. Mayer, *Organometallics* **1994**, *13*, 322–331.
[109] W. A. de Jong, L. Visscher, W. C. Nieuwpoort, *J. Mol. Struct.: THEOCHEM* **1999**, *458*, 41–52; corrigendum *J. Mol. Struct.: THEOCHEM* **2002**, *581*, 259.
[110] J. V. Ortiz, *Chem. Phys. Lett.* **1998**, *296*, 494–498.
[111] S. Petrie, *J. Chem. Phys.* **1997**, *107*, 3042–3055.
[112] L. Shao, S. M. Sickafoose, J. D. Langenberg, D. J. Brugh, M. D. Morse, *J. Chem. Phys.* **2000**, *112*, 4118–4123.
[113] P. Kramkowski, G. Baum, U. Radius, M. Kaupp, M. Scheer, *Chem. Eur. J.* **1999**, *5*, 2890–2898.
[114] Y. Do, R. H. Holm, *Inorg. Chim. Acta* **1985**, *104*, 33–40.
[115] A. Nowek, J. Leszczynski, *J. Phys. Chem.* **1994**, *98*, 13210–13214.
[116] S. A. Beaton, M. C. L. Gerry, *J. Chem. Phys.* **1999**, *110*, 10715–10724.
[117] L. Pu, B. Twamley, S. T. Haubrich, M. M. Olmstead, B. V. Mork, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 650–656.
[118] P. P. Power, *Chem. Commun.* **2003**, 2091–2101.
[119] D. Weiss, M. Winter, K. Merz, A. Knuefer, R. A. Fischer, N. Fröhlich, G. Frenking, *Polyhedron* **2002**, *21*, 535–542.
[120] C.-H. Lai, M.-D. Su, S.-Y. Chu, *Polyhedron* **2002**, *21*, 579–585.
[121] R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 11966–11967.
[122] R. Breidohr, O. Shestakov, D. K. Setzer, H. E. Fink, *J. Mol. Spectrosc.* **1995**, *172*, 369–377.
[123] A. C. Filippou, A. I. Philippopoulos, G. Schnakenburg, *Organometallics* **2003**, *22*, 3339–3341.
[124] M. Barysz, P. Pyykkö, *Chem. Phys. Lett.* **2003**, *368*, 538–541.
[125] M. Urban, G. H. F. Diercksen, M. Jurek, *Mol. Phys.* **1998**, *94*, 199–208.
[126] T. Ziegler, *J. Am. Chem. Soc.* **1983**, *105*, 7543–7549.
[127] R. Wiest, A. Strich, J. Demuynck, M. Benard, P. E. M. Siegbahn, *Chem. Phys. Lett.* **1985**, *122*, 453–458.

Received: December 17, 2004
Published online: April 14, 2005