

# AM1\* parameters for palladium and silver

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**Abstract** We report the parameterization of AM1\* for the elements palladium and silver. The basis sets for both metals contain one set each of *s*-, *p*- and *d*-orbitals. AM1\* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Zr, Mo, Pd, Ag, I and Au. The performance and typical errors of AM1\* are discussed for Pd and Ag and compared with the PM6 Hamiltonian.

**Keywords** AM1\* · Palladium parameters · Semiempirical MO theory · Silver parameters

## Introduction

We have introduced AM1\* [1–9] as an extension of AM1 [10] that uses *d*-orbitals for the elements P, S, Cl [1], Al, Si, Ti and Zr [2], Cu and Zn [3], Br and I [4], V and Cr [5], Co and Ni [6], Mn and Fe [8], and Au [7]. The AM1\* parameters for molybdenum are based on Voityuk and Röscher's AM1(d) parameter set [11], extended to include the

AM1\* core–core parameters for interactions between Mo and new AM1\* elements. The rationalization behind AM1\* is to retain the advantages of AM1 (good energies for hydrogen bonds, higher rotation barriers for  $\pi$ -systems than MNDO [12, 13] or PM3 [14–16]) for the first-row elements, improve the performance over AM1 for compounds that contain second-row and heavier elements, and provide a published parameterization for an AM1-like method for the transition metals. As a continuation of this work, we now report AM1\* parameters for palladium and silver. Both palladium and silver are important for organometallic chemistry and biological systems [17–20].

## Theory

AM1\* for the two new elements uses the same basic theory as outlined previously [1, 2]. As for other element–H interactions, the core–core repulsion potentials for the Pd–H and Ag–H interactions use a distance-dependent term  $\delta_{ij}$ , rather than the constant term used for core–core potentials for most other interactions in AM1\* [1]. This distance-dependent  $\delta_{ij}$  was also used for the Mo–H interaction in AM1(d) [11] and for Ti–H, V–H, Cr–H, Mn–H, Fe–H, Co–H, Ni–H, Cu–H, Zn–H, Br–H, Zr–H, Mo–H, I–H and Au–H in AM1\* [2–9]. The core–core terms for Pd–H and Ag–H are thus

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 [1 + r_{ij} \delta_{ij} \exp(-\alpha_{ij} r_{ij})], \quad (1)$$

where all terms have the same meaning as in [1]. The standard MNDO/d formula is used for all other core–core interactions:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 [1 + \delta_{ij} \exp(-\alpha_{ij} r_{ij})]. \quad (2)$$

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The parameterization techniques used were the same as those reported in [1] and [2], and will not be described further here.

### Parameterization data

The target values used for parameterization and their sources are defined in Tables S1, S2 and S3 of the “Electronic supplementary material” (ESM). We have used heats of formation, Koopmans’ theorem ionization potentials, dipole moments and geometrical variables, as we did for the Ti and Zr, Cu and Zn, Br and I, V and Cr, Mn and Fe, Co and Ni, and Au parameterizations [2–9]. Because the experimental data for the heats of formation of compounds of these two metals are relatively sparse, we have also extended our parameterization data using a small series of model compounds whose heats of formation were derived by us from DFT calculations [21]. As before [1–9], we checked that experimental values for heats of formation were reasonable using DFT calculations.

DFT calculations used the Gaussian 03 suite of programs [22] with the LANL2DZ basis set and standard effective core potentials [23–26] augmented by a set of polarization functions [27] (designated LANL2DZ + pol) and the B3LYP hybrid functional [28–30].

Experimental parameterization data for palladium and silver were taken largely from the NIST Webbook [31], but also from the OpenMopac collection [32] and the other experimental and theoretical sources given in the “ESM.”

The energetic parameterization data and their sources are given in Table S1 of the “ESM.” In addition to the energetic data, geometries, dipole moments and ionization potentials taken from the above sources as well as crystal structures from the Cambridge Structural Database (CSD) [33] were used in the parameterization to ensure that not only the energetic and electronic properties of the “prototype” compounds but also the structures of large palladium and silver compounds were well replicated.

### Results

Table 1 shows the optimized AM1\* parameters. Geometries were optimized with the new AM1\* parameterization using VAMP 10.0 [34], while the PM6 calculations used MOPAC2009 [35]. We have presented the related errors for each property (heats of formation, ionization potentials, dipole moments, and geometries) as mean unsigned errors (MUEs) and mean signed errors (MSEs). MUE is used to measure how close predictions are to the experimental values, whereas MSE indicates the direction of deviation of the predictions from the experimental outcomes.

**Table 1** AM1\* parameters for the elements Pd and Ag

Parameter	Pd	Ag
$U_{ss}$ (eV)	−76.260000	−33.8199198
$U_{pp}$ (eV)	−39.017218	−42.1012517
$U_{dd}$ (eV)	−85.301000	−38.9320154
$\zeta_s$ (bohr <sup>−1</sup> )	4.9532701	2.7553222
$\zeta_p$ (bohr <sup>−1</sup> )	1.8966327	1.3780158
$\zeta_d$ (bohr <sup>−1</sup> )	1.9466532	12.2012509
$\beta_s$ (eV)	−15.4166941	−18.1474276
$\beta_p$ (eV)	−22.4925053	−1.7680918
$\beta_d$ (eV)	−9.3228885	−30.8685962
$g_{ss}$ (eV)	7.041000	6.4097588
$g_{pp}$ (eV)	9.3779172	58.3766967
$g_{sp}$ (eV)	3.6756901	7.8308751
$g_{p2}$ (eV)	10.300000	23.2069891
$h_{sp}$ (eV)	0.095300	0.0007129
$z_{sn}$ (bohr <sup>−1</sup> )	2.793000	1.0922285
$z_{pn}$ (bohr <sup>−1</sup> )	6.158780	5.0875757
$z_{dn}$ (bohr <sup>−1</sup> )	1.630913	0.5420887
$\rho(\text{core})$ (bohr <sup>−1</sup> )	1.4877993	4.1795381
$\Delta H_f^\circ(\text{atom})$ (kcal mol <sup>−1</sup> )	90.0	68.1
$F_{sd}^0$ (eV)	7.900000	2.8448763
$G_{sd}^2$ (eV)	2.613148	2.1370680
$\alpha(ij)$		
H	2.3317788	2.8342282
C	2.9390125	2.7215778
N	2.5743398	3.2932884
O	2.8057742	3.5121360
F	3.5990816	1.8343208
Al	1.9512741	2.0535270
Si	1.9261566	1.7508697
P	1.7991086	1.7947819
S	2.2453993	2.7887233
Cl	3.0022618	3.7655720
Ti	1.9343017	1.3326531
V	2.4540320	2.4123900
Cr	1.9673238	1.6773407
Mn	2.3168660	1.0563564
Fe	2.3857968	2.4413565
Co	2.1511338	3.0050953
Ni	3.0845276	3.2019364
Cu	1.5305052	1.8746527
Zn	4.9294752	1.9842120
Br	2.7086960	3.9190319
Zr	2.0165668	1.3500000
Mo	1.6804214	1.6133712
Pd	2.5728472	1.9319955
Ag	1.9319955	1.8599139
I	2.6703530	2.0149744
Au	2.1441945	1.9932217
$\delta(ij)$		

**Table 1** (continued)

Parameter	Pd	Ag
H	-1.3432500	-5.4225162
C	8.1048287	6.3070555
N	2.7572129	13.6248570
O	3.1500546	16.6099871
F	14.9012342	0.8868232
Al	2.2512207	5.1064811
Si	1.3483759	1.9420108
P	1.6338617	1.8515105
S	2.4879360	4.8652263
Cl	11.5803705	112.9986605
Ti	1.6042935	1.2144293
V	6.5094095	9.5836752
Cr	1.7827148	1.3872944
Mn	2.0267985	0.3870326
Fe	4.2154439	7.8707061
Co	2.4923551	14.3857882
Ni	13.3605349	13.0954848
Cu	0.3917107	1.2113191
Zn	87.9255763	1.6710565
Br	5.8174674	159.3996013
Zr	1.4839490	1.7179617
Mo	1.3163647	1.9549661
Pd	6.2302938	1.6902714
Ag	1.6902714	1.8502457
I	4.7869339	1.6868259
Au	2.2146414	1.7832981

## Palladium

### Heats of formation

We have presented the calculated heats of formation for our training set of palladium compounds in Table 2, and compared our results with those obtained using Stewart's published PM6 method [36].

The AM1\* parameterization data set contains 84 compounds, of which 47 are taken from the original PM6 parameterization data set. AM1\* performs significantly better for its extended training set, with an MUE of 18.2 kcal mol<sup>-1</sup>, compared with 26.6 kcal mol<sup>-1</sup> for PM6. PM6 produces especially large errors for the compounds that were not included in its original training set. On the other hand, PM6 performs better for the subset for which it was trained. The MUEs for the PM6 training subset are found to be 21.8 kcal mol<sup>-1</sup> and 11.7 kcal mol<sup>-1</sup> for AM1\* and PM6, respectively. These data convincingly demonstrate the influence of the extent of the training data. This situation results from the limited amount of data available

for parameterizing semiempirical MO techniques for transition metals. AM1\* underestimates the heats of formation of palladium-containing compounds by -4.5 kcal mol<sup>-1</sup> (MSE), whereas PM6 tends to give smaller positive systematic errors for palladium-containing compounds (MSE = +2.5 kcal mol<sup>-1</sup>).

The molecules that give the largest positive errors for AM1\* are PdCl<sub>2</sub> (61.0 kcal mol<sup>-1</sup>), PdC<sub>9</sub>N<sub>4</sub>H<sub>12</sub>Br<sub>2</sub> (CH<sub>2</sub>((NC<sub>2</sub>H<sub>2</sub>)(NCH<sub>3</sub>)C)<sub>2</sub>PdBr<sub>2</sub>, AMIPER) (56.9 kcal mol<sup>-1</sup>), PdBr<sub>2</sub> (53.0 kcal mol<sup>-1</sup>) and PdC<sub>36</sub>P<sub>2</sub>H<sub>30</sub>Cl<sub>2</sub> (*cis*-Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>) (52.4 kcal mol<sup>-1</sup>). The largest negative errors are found for PdCl<sub>6</sub><sup>2-</sup> (-122.9 kcal mol<sup>-1</sup>), PdC<sub>10</sub>N<sub>2</sub>H<sub>8</sub>Cl<sub>4</sub> ((C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>PdCl<sub>4</sub>, BOKHAK) (-67.0 kcal mol<sup>-1</sup>), PdMe<sub>2</sub><sup>+</sup> (-58.3 kcal mol<sup>-1</sup>), PdMe<sub>2</sub> (-53.9 kcal mol<sup>-1</sup>), and PdC<sub>2</sub>H<sub>2</sub><sup>+</sup> (-49.1 kcal mol<sup>-1</sup>). As before [3–9], the fact that AM1\* uses the unchanged AM1 parameterization for the elements H, C, N, O and F limits the possible accuracy of the parameterization. The large errors for the compounds containing these elements are not surprising. As found for other metals, the large errors in pure AM1\* element-containing compounds, such as PdCl<sub>2</sub>, PdCl<sub>6</sub><sup>2-</sup> and PdBr<sub>2</sub>, are likely to be a consequence of our sequential parameterization strategy, in contrast to the simultaneous parameterization used for PM6 [36].

### Ionization potentials and dipole moments

Table 3 shows a comparison of the calculated and experimental Koopmans' theorem ionization potentials and dipole moments for AM1\* and PM6.

AM1\*, with an MUE of 0.64 eV, performs better than PM6 (MUE of 1.99 eV) for Koopmans' theorem ionization potentials. Both AM1\* and PM6 tend to underestimate ionization potentials for palladium-containing compounds. However, this tendency is more serious for PM6, with an MSE of -1.99 eV, compared with the AM1\* MSE of -0.47 eV.

Large AM1\* errors are found for PdO (-1.34 eV) and Pd (-0.90 eV). However, PM6 produces very large errors for all four compounds used in the training set. Although these data are available in NIST [31], they were not used in the original PM6 parameterization. The large PM6 errors are thus to be expected.

AM1\*, with an MSE of 0.08 debyes, shows no significant tendency to produce systematic errors for dipole moments of palladium compounds, whereas PM6 gives a negative systematic error of -0.39 debyes (MSE). AM1\* and PM6 perform comparably, with MUEs of 0.97 and 1.02 debyes, respectively. Large AM1\* errors are found in particular for halogen-containing palladium compounds. These are PdC<sub>8</sub>H<sub>20</sub>S<sub>2</sub>Cl<sub>2</sub> (*trans*-Pd(Cl)<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>) (2.30 debyes), PdBr<sub>2</sub> (1.79 debyes), PdI<sub>2</sub> (-1.63 debyes), and PdC<sub>4</sub>N<sub>2</sub>H<sub>6</sub>Cl<sub>2</sub> (PdCl<sub>2</sub>(MeCN)<sub>2</sub>) (1.52 debyes). However, PM6 also gives erroneous results for the fluorides and chlorides of palladium.

**Table 2** Calculated AM1\* and PM6 heats of formation and errors compared with our target values for the palladium-containing compounds used to parameterize AM1\* (all values are in kcal mol<sup>-1</sup>). Errors lower than 10 kcal mol<sup>-1</sup> are shown in regular font, errors of 10–20 kcal mol<sup>-1</sup>

are shown in italics, and errors greater than 20 kcal mol<sup>-1</sup> are shown in bold. Codenames within parentheses indicate the CSD names [33] of the compounds

Compound	Target $\Delta H_f^\circ$	AM1*		PM6	
		$\Delta H_f^\circ$	Error	$\Delta H_f^\circ$	Error
Pd	90	90.0	0.0	84.8	-5.2
Pd <sup>-</sup>	77.4	77.5	0.1	119.8	42.3
Pd <sub>2</sub>	168.5	159.3	-9.2	188.8	20.3
Pd <sub>2</sub> <sup>-</sup>	118.1	122.3	4.2	168.4	50.3
PdH <sub>2</sub>	74.5	79.7	5.2	32.2	-42.3
PdH	91.7	97.9	6.2	79.8	-11.9
PdH <sup>+</sup>	300	305.2	5.2	253.2	-46.8
PdCH <sub>3</sub>	109.7	83.1	-26.6	75.5	-34.2
PdCH <sub>3</sub> <sup>+</sup>	295.9	262.6	-33.4	238.7	-57.2
Pd(H)CH <sub>3</sub>	107.9	82.5	-25.4	61.6	-46.3
PdC <sub>2</sub> H <sub>2</sub> <sup>+</sup>	336.9	287.8	-49.1	246.4	-90.5
PdMe <sub>2</sub>	127.4	73.6	-53.9	57.3	-70.1
PdMe <sub>2</sub> <sup>+</sup>	316	257.7	-58.3	212.7	-103.3
Pd <sub>2</sub> Me <sub>2</sub>	133.2	147.8	14.6	117.2	-16.0
PdC <sub>8</sub> H <sub>10</sub> (ALCPPD10)	69.5	52.4	-17.1	72.1	2.6
Pd(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	333.2	346.0	12.8	341.3	8.1
Pd(CN) <sub>4</sub> <sup>2-</sup> (EATCPD)	117.3	79.1	-38.2	138.2	20.9
PdC <sub>8</sub> N <sub>4</sub> H <sub>12</sub> <sup>2+</sup> (KUXSIF)	443.9	400.7	-43.3	410.9	-33
PdC <sub>12</sub> N <sub>4</sub> H <sub>8</sub> (JARCEK)	144.2	146.1	1.9	159.3	15.1
Pd(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	303.3	301.7	-1.6	321.4	18.1
PdO <sup>-</sup>	49.17	27.2	-22.0	88.5	39.4
Pd(H)OH	3.25	15.4	12.2	26.9	23.7
PdC <sub>2</sub> H <sub>6</sub> O (Methyl methoxy palladium)	18	1.6	-16.4	23.1	5.1
Pd(H <sub>2</sub> O) <sub>4</sub> <sup>2+</sup>	183.9	201.9	18.0	200.1	16.2
Pd(CO) <sub>4</sub>	-87.1	-83.5	3.6	-89.9	-2.8
PdC <sub>6</sub> H <sub>17</sub> O <sub>4</sub> (Pd(II)(Me <sub>2</sub> O)(OMe)(H <sub>2</sub> O)(Me <sub>2</sub> CO))	-26.4	-54.4	-28.0	-45.6	-19.2
PdC <sub>10</sub> N <sub>2</sub> H <sub>8</sub> O <sub>4</sub> (EWOSUE)	-33.3	-25.2	8.1	-17.5	15.8
PdC <sub>12</sub> N <sub>4</sub> H <sub>10</sub> O <sub>4</sub> (BZQXPD01)	55.5	65.0	9.5	62.9	7.4
PdC <sub>4</sub> N <sub>8</sub> H <sub>9</sub> O <sub>4</sub> (BETWEC)	42.9	47.2	4.3	54.1	11.2
PdC <sub>4</sub> O <sub>8</sub> <sup>2-</sup> (Pd(II)(Ox) <sub>2</sub> <sup>2-</sup> (FOVMUY))	-359.1	-401.2	-42.1	-351.7	7.4
PdC <sub>10</sub> N <sub>2</sub> H <sub>12</sub> O <sub>8</sub> (Palladium EDTA)	-322.7	-364.5	-41.8	-362.9	-40.2
Pd <sub>2</sub> C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> (Pd <sub>2</sub> (Cp) <sub>2</sub> (CO) <sub>2</sub> )	36.5	34.1	-2.4	48.2	11.7
PdF	40.8	32.5	-8.3	31.2	-9.6
Pd(H)F	49.3	28.5	-20.8	14.4	-34.9
PdCH <sub>3</sub> F	2.7	16.7	14.0	10.6	7.9
PdF <sub>2</sub>	-38.5	-38.9	-0.4	-29.4	9.1
PdF <sub>4</sub> <sup>2-</sup>	-156.7	-156.7	0.0	-152.1	4.6
PdAlH	102.9	120.4	17.5	162.5	59.6
Pd(AlH) <sub>2</sub>	141.5	135.4	-6.1	235.0	93.5
PdSi	134.7	134.7	0.0	160.9	26.2
PdP <sup>+</sup>	316	300.4	-15.6	273.3	-42.7
PdP <sup>-</sup>	84.3	88.4	4.1	99.0	14.7
PdS	108.8	97.8	-11.0	87.4	-21.4
PdC <sub>6</sub> N <sub>6</sub> H <sub>6</sub> S <sub>3</sub> O (CAXQUN)	115.1	85.4	-29.7	55.1	-60.0
PdC <sub>4</sub> N <sub>4</sub> H <sub>6</sub> S <sub>4</sub> (LESSIL)	50.3	50.5	0.2	78.6	28.3
PdC <sub>10</sub> N <sub>4</sub> H <sub>2</sub> O <sub>8</sub> S <sub>4</sub> (BEWKAP)	73.5	70.9	-2.6	77.4	3.9
PdC <sub>4</sub> N <sub>6</sub> H <sub>8</sub> S <sub>4</sub> (DTHBPD10)	34.6	44.6	10.0	47.3	12.7
PdCl	60.2	86.3	26.1	42.8	-17.4
Pd(H)Cl	64.9	68.7	3.8	31.0	-33.9

**Table 2** (continued)

PdCH <sub>3</sub> Cl	23.2	65.8	42.6	24.7	1.5
PdCl <sub>2</sub>	0.6	61.6	61.0	6.1	5.5
Pd <sub>2</sub> C <sub>6</sub> H <sub>10</sub> Cl <sub>2</sub> (pi-Allyl palladium chloride dimer)	4.4	-28.1	-32.5	4	-0.4
PdC <sub>8</sub> H <sub>12</sub> Cl <sub>2</sub> (CYOCPD02)	-18.9	-30.5	-11.6	-41	-22.1
PdC <sub>4</sub> N <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> (FEQCOT)	10.4	10.9	0.5	-4.6	-15.0
PdC <sub>4</sub> N <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> (PdCl <sub>2</sub> (MeCN) <sub>2</sub> )	-3.8	13.8	17.6	5.6	9.4
PdC <sub>4</sub> N <sub>2</sub> H <sub>12</sub> Cl <sub>2</sub> (AMBUPD)	-62.1	-36.6	25.5	-52.9	9.2
PdC <sub>11</sub> N <sub>2</sub> H <sub>10</sub> Cl <sub>2</sub> O (BATTIZ)	-60.1	-51.9	8.2	-63	-2.9
PdC <sub>36</sub> P <sub>2</sub> H <sub>30</sub> Cl <sub>2</sub> (cis-Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> )	122.1	174.5	52.4	121.5	-0.6
PdC <sub>8</sub> H <sub>20</sub> S <sub>2</sub> Cl <sub>2</sub> (trans-Pd(Cl) <sub>2</sub> (SEt <sub>2</sub> ) <sub>2</sub> )	-102.5	-93.4	9.1	-98.4	4.1
Pd(CO)Cl <sub>3</sub> <sup>-</sup> (KATPEA)	-151.7	-153.7	-2.0	-154.8	-3.1
PdCl <sub>4</sub>	-106.4	-104.2	2.2	-117.5	-11.1
PdCl <sub>4</sub> <sup>2-</sup> (AVUKOR)	-119.7	-119.4	0.3	-117.6	2.1
PdC <sub>10</sub> N <sub>2</sub> H <sub>8</sub> Cl <sub>4</sub> ((C <sub>3</sub> H <sub>4</sub> N) <sub>2</sub> PdCl <sub>4</sub> , BOKHAK)	3.5	-63.5	-67.0	-5.3	-8.8
PdCl <sub>6</sub> <sup>2-</sup> (JIZLOT)	-149.9	-272.8	-122.9	-174.1	-24.2
PdTi	103.3	102.3	-1.0	114.0	10.7
PdV	110.4	110.4	0.0	207.8	97.4
PdCr	160.2	159.8	-0.4	200.1	39.9
PdMn	86.2	86.2	0.0	157.4	71.2
PdFe	142.9	142.9	0.0	188.2	45.3
PdCo	165.3	165.3	0.0	101.9	-63.4
PdNi	100.2	100.2	0.0	190.9	90.7
PdCu	138.8	138.8	0.0	187.9	49.1
PdZn	98.4	119.4	21.0	79.6	-18.8
PdBr <sub>2</sub>	5.6	58.6	53.0	10.9	5.3
PdC <sub>9</sub> N <sub>4</sub> H <sub>12</sub> Br <sub>2</sub> (CH <sub>2</sub> ((NC <sub>2</sub> H <sub>2</sub> )(NCH <sub>3</sub> )C) <sub>2</sub> PdBr <sub>2</sub> , AMIPER)	50.2	107.1	56.9	52	1.8
Pd(CO)Br <sub>3</sub> <sup>-</sup> (KATPIE)	-133.1	-132.6	0.5	-131.1	2.0
PdBr <sub>4</sub>	-92.3	-121.0	-28.7	-95.3	-3.0
PdBr <sub>4</sub> <sup>2-</sup> (FETHOB)	-98.9	-127.8	-28.9	-95.3	3.6
PdZr	172.9	129.0	-43.9	232.4	59.5
PdMo	221.9	221.9	0.0	243.2	21.3
PdAg <sub>2</sub>	186.5	186.5	0.0	227.1	40.6
PdI <sub>2</sub>	16.3	59.1	42.8	30.1	13.8
PdI <sub>4</sub> <sup>2-</sup>	-68.3	-68.31	0.0	-52.6	15.7
PdAu <sub>2</sub>	215	202.7	-12.3	263.6	48.6
			<b>AMI*</b>	<b>PM6</b>	
<i>N</i> =84					
<b>Most positive error</b>			61.0	97.4	
<b>Most negative error</b>			-122.9	-103.3	
<b>MSE</b>			-4.5	2.5	
<b>MUE</b>			18.2	26.6	
<b>RMSD</b>			28.1	36.7	
<b>Results for the PM6 parameterization set (N=47)</b>					
<b>MSE</b>			-1.9	0.3	
<b>MUE</b>			21.8	11.7	
<b>RMSD</b>			32.6	16.2	

**Table 3** Calculated AM1\* and PM6 Koopmans' theorem ionization potentials and dipole moments for palladium-containing compounds. The errors are coded by font style: errors of up to 0.5 eV or 0.5 debyes

are shown in regular font, errors of between 0.5 and 1.0 are shown in italics, and errors of larger than 1.0 are shown in bold

Compound	Target	AM1*		PM6	
			Error		Error
<b>Koopmans' Theorem Ionization Potentials for Palladium Compounds (eV)</b>					
Pd	8.34	7.44	-0.90	7.46	-0.87
Pd <sub>2</sub>	7.70	7.94	0.24	6.58	-1.12
PdO	9.76	8.42	-1.34	6.43	-3.33
PdSi	8.40	8.50	0.10	5.75	-2.65
		<b>AM1*</b>		<b>PM6</b>	
<i>N=4</i>					
MSE		-0.47		-1.99	
MUE		0.64		1.99	
<b>Dipole Moments for Palladium Compounds (Debye)</b>					
PdCH <sub>3</sub>	1.03	1.56	0.53	1.03	0.00
PdCH <sub>3</sub> <sup>+</sup>	1.19	0.94	-0.25	1.05	-0.13
Pd(H)CH <sub>3</sub>	1.65	2.73	1.08	0.68	-0.97
PdC <sub>2</sub> H <sub>2</sub> <sup>+</sup>	0.76	0.99	0.23	0.72	-0.04
PdMe <sub>2</sub> <sup>+</sup>	0.69	0.74	0.05	0.35	-0.34
PdC <sub>2</sub> H <sub>6</sub> O (Methyl methoxy palladium(II))	1.68	2.01	0.33	2.62	0.94
PdCH <sub>3</sub> F	4.63	3.50	-1.13	3.41	-1.22
PdF	4.73	4.23	-0.50	2.86	-1.87
Pd(H)F	4.24	3.21	-1.03	0.02	-4.22
PdCH <sub>3</sub> Cl	6.16	5.30	-0.86	4.66	-1.50
PdCl <sub>2</sub>	3.66	2.40	-1.26	4.68	1.02
PdC <sub>4</sub> N <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> (PdCl <sub>2</sub> (MeCN) <sub>2</sub> )	11.32	12.84	1.52	13.02	1.70
PdC <sub>8</sub> H <sub>20</sub> S <sub>2</sub> Cl <sub>2</sub> (trans-Pd(Cl) <sub>2</sub> (SEt <sub>2</sub> ) <sub>2</sub> )	1.65	3.95	2.30	2.50	0.85
PdBr <sub>2</sub>	3.03	4.82	1.79	3.26	0.23
PdI <sub>2</sub>	2.38	0.75	-1.63	2.05	-0.33
		<b>AM1*</b>		<b>PM6</b>	
<i>N=15</i>					
MSE		0.08		-0.39	
MUE		0.97		1.02	

## Geometries

Table 4 shows a comparison of AM1\* and PM6 results in reproducing the geometries of the palladium-containing compounds.

Both AM1\* and PM6 tend to overestimate bond lengths to the metal for palladium-containing compounds. How-

ever, this tendency is much more serious for PM6, with an MSE of 0.24 Å, than for AM1\*, with an MSE of 0.05 Å. AM1\*, with an MUE of 0.09 Å, performs significantly better than PM6 (MUE of 0.31 Å) for bond lengths to palladium. Once again [7], we find that PM6 predicts bond lengths to be very long for the diatomic transition metal compounds. The PM6 parameterization dataset does not

**Table 4** Calculated AM1\* and PM6 bond lengths and angles for palladium-containing compounds. The codenames within parentheses indicate the CSD names [33] of the compounds. The errors are coded

by font style as follows: errors of up to 0.05 Å or 0.5° are shown in regular font, errors of between 0.05 and 0.1 Å or 0.5 and 1.0° are shown in italics, errors of larger than 0.1 Å or 1° are shown in bold

Compound	Variable	Target	AM1*		PM6	
				Error		Error
Pd <sub>2</sub>	Pd-Pd	2.74	2.49	-0.25	2.31	-0.43
Pd <sub>2</sub> <sup>-</sup>	Pd-Pd	2.67	2.58	-0.10	2.51	-0.16
PdH <sup>+</sup>	Pd-H	1.52	1.50	-0.02	1.53	0.01
PdH	Pd-H	1.54	1.54	0.00	1.53	-0.01
PdH <sub>2</sub>	Pd-H	1.53	1.54	0.01	1.79	0.26
	H-Pd-H	68.0	80.9	12.9	27.0	-41.0
PdCH <sub>3</sub> <sup>+</sup>	Pd-C	2.00	2.27	0.27	2.00	0.00
PdCH <sub>3</sub>	Pd-C	2.00	2.23	0.23	2.03	0.03
PdCH <sub>4</sub>	Pd-C	2.00	2.22	0.22	2.02	0.02
	H-Pd-C	87.0	82.6	-4.4	85.3	-1.7
PdC <sub>2</sub> H <sub>2</sub> <sup>+</sup>	Pd-C	2.48	2.53	0.04	2.09	-0.39
PdMe <sub>2</sub> <sup>+</sup>	Pd-C	2.03	2.18	0.15	2.01	-0.02
	C-Pd-C	93.5	144.3	50.8	94.0	0.5
PdMe <sub>2</sub>	Pd-C	2.00	2.16	0.16	2.03	0.03
	C-Pd-C	89.9	151.7	61.8	94.3	4.4
Pd <sub>2</sub> (Me) <sub>2</sub>	Pd-Pd	2.64	2.51	-0.13	2.62	-0.02
	Pd-C	2.07	2.20	0.13	2.01	-0.06
PdC <sub>4</sub> H <sub>8</sub> (Pd(-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -))	Pd-C	2.03	2.23	0.20	2.00	-0.03
	C-Pd-C	85.3	81.5	-3.8	87.9	2.6
PdC <sub>8</sub> H <sub>10</sub> (Pd(Cp)C <sub>3</sub> H <sub>5</sub> (ALCPPD10))	Pd-C	2.27	2.44	0.17	2.40	0.13
	Pd-C	2.07	2.11	0.04	2.16	0.09
	Pd-C	2.25	2.34	0.09	2.30	0.05
PdC <sub>9</sub> N <sub>2</sub> H <sub>21</sub> <sup>-</sup> (BEHMIK)	Pd-N	2.15	2.02	-0.13	2.10	-0.05
	N-Pd-N	84.5	89.1	4.6	79.3	-5.3
	Pd-C	2.15	2.26	0.11	2.40	0.25
Pd(NH <sub>3</sub> ) <sub>4</sub>	Pd-N	2.14	2.18	0.03	2.15	0.01
Pd(CN) <sub>4</sub>	Pd-C	2.00	2.13	0.13	1.96	-0.04
Pd(CN) <sub>4</sub> <sup>2-</sup> (EATCPD)	Pd-C	2.00	2.16	0.16	2.00	0.00
	C-N	1.15	1.17	0.02	1.17	0.02
PdC <sub>8</sub> N <sub>4</sub> H <sub>12</sub> <sup>2+</sup> (KUXSIF)	Pd-N	1.96	2.06	0.10	1.99	0.03
	C-N	1.08	1.16	0.08	1.15	0.07
	C-C	1.49	1.44	-0.05	1.44	-0.05
PdC <sub>10</sub> N <sub>4</sub> H <sub>20</sub> <sup>2+</sup> (BUXSIW)	Pd-N	2.05	1.95	-0.10	1.95	-0.10
	N-Pd-N	83.1	83.4	0.2	84.3	1.2
PdC <sub>12</sub> N <sub>4</sub> H <sub>8</sub> (JARCEK)	Pd-N	1.94	2.11	0.17	2.18	0.24
	N-Pd-N	84.3	79.9	-4.5	77.7	-6.6
	Pd-C	2.12	2.15	0.03	1.92	-0.20
Pd(NH <sub>3</sub> ) <sub>6</sub>	Pd-N	2.08	2.20	0.12	2.33	0.25
	Pd-N'	2.56	2.28	-0.28	2.34	-0.22
Pd(H)(OH)	Pd-H	1.52	1.55	0.03	1.52	0.00
	Pd-O	1.92	1.94	0.02	1.90	-0.02
	H-Pd-O	93.2	143.5	50.3	81.2	-12.0
PdCO	Pd-C	1.89	2.12	0.23	1.83	-0.06
PdC <sub>2</sub> H <sub>6</sub> O (Methyl methoxy palladium(II))	Pd-O	2.04	1.92	-0.12	2.16	0.12
	Pd-C	2.08	2.14	0.06	2.04	-0.04
PdO <sub>2</sub>	Pd-O	2.07	2.07	0.00	2.07	0.00
Pd(H <sub>2</sub> O) <sub>4</sub> <sup>2+</sup>	Pd-O	2.11	2.11	0.00	2.04	-0.07
Pd(CO) <sub>4</sub>	Pd-C	2.06	2.17	0.11	2.14	0.08
PdC <sub>6</sub> H <sub>17</sub> O <sub>4</sub> (Pd(II)(Me <sub>2</sub> O)(OMe)(H <sub>2</sub> O)(Me <sub>2</sub> CO))	Pd-O(H <sub>2</sub> O)	2.25	2.25	0.00	2.20	-0.05

Table 4 (continued)

	Pd-O(Me <sub>2</sub> O)	2.18	2.22	0.04	2.04	-0.14
	Pd-O(MeO)	1.97	2.03	0.06	1.92	-0.05
	Pd-O(Me <sub>2</sub> CO)	2.13	2.04	-0.09	2.05	-0.08
PdC <sub>10</sub> N <sub>2</sub> H <sub>8</sub> O <sub>4</sub> (EWOSUE)	Pd-O	1.98	2.08	0.10	2.00	0.02
	O-Pd-O	83.1	75.9	-7.2	84.1	1.0
PdC <sub>12</sub> N <sub>4</sub> H <sub>10</sub> O <sub>4</sub> (BZQXPD01)	Pd-N	1.96	2.05	0.09	1.98	0.02
	N-Pd-N	79.5	81.6	2.1	83.6	4.1
PdC <sub>4</sub> N <sub>8</sub> H <sub>9</sub> O <sub>4</sub> (BETWEC)	Pd-N	1.96	2.05	0.09	1.98	0.02
	N-Pd-N	79.3	80.5	1.2	83.8	4.5
PdC <sub>4</sub> O <sub>4</sub> <sup>2-</sup> (Pd(II)(Ox) <sub>2</sub> <sup>2-</sup> (FOVMUY))	Pd-O	1.98	2.08	0.10	2.01	0.03
	O-Pd-O	85.0	72.4	-12.6	84.3	-0.8
PdC <sub>10</sub> N <sub>2</sub> H <sub>12</sub> O <sub>8</sub> (Palladium EDTA)	Pd-N	2.71	2.32	-0.39	2.11	-0.60
	N-Pd-N	67.4	77.8	10.5	86.4	19.0
	Pd-O	2.17	2.16	-0.01	2.34	0.17
Pd <sub>2</sub> C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> (Pd <sub>2</sub> (Cp) <sub>2</sub> (CO) <sub>2</sub> )	Pd-Pd	2.75	2.63	-0.12	3.17	0.42
	Pd-C(C=O)	2.04	2.25	0.21	2.09	0.05
	Pd-Pd-C	47.7	54.0	6.3	40.9	-6.8
	C=O	1.18	1.18	0.00	1.16	-0.02
	Pd-C	2.41	2.39	-0.02	2.33	-0.08
PdF	Pd-F	2.01	2.01	0.00	1.96	-0.05
PdHF	Pd-F	1.95	2.02	0.07	1.93	-0.02
	Pd-H	1.49	1.53	0.04	1.53	0.04
	F-Pd-H	90.7	140.6	49.9	90.0	-0.7
PdCH <sub>3</sub> F	Pd-C	2.06	2.14	0.08	2.04	-0.02
	Pd-F	2.01	2.00	-0.01	1.94	-0.07
PdF <sub>2</sub>	Pd-F	1.94	1.98	0.04	1.96	0.02
PdF <sub>4</sub>	Pd-F	2.06	2.08	0.02	2.05	-0.01
PdAlH	Pd-Al	2.23	2.23	0.00	3.96	1.73
Pd(AlH) <sub>2</sub>	Pd-Al	2.39	2.37	-0.01	3.99	1.61
PdSi	PdSi	2.14	2.14	0.00	2.27	0.13
PdP <sup>+</sup>	Pd-P	2.15	2.19	0.04	2.03	-0.12
PdP <sup>-</sup>	Pd-P	2.17	2.28	0.11	2.17	0.00
PdSi <sub>2</sub> P <sub>2</sub> H <sub>12</sub> (cis-Pd(PH <sub>3</sub> ) <sub>2</sub> (SiH <sub>3</sub> ) <sub>2</sub> )	Pd-P	2.44	2.43	-0.01	2.35	-0.09
	P-Pd-P	102.1	105.2	3.1	178.8	76.7
	Pd-Si	2.41	2.57	0.16	3.47	1.06
	Si-Pd-Si	74.4	116.2	41.8	38.7	-35.7
PdS	Pd-S	2.22	2.25	0.03	2.06	-0.16
PdS <sub>2</sub>	Pd-S	2.28	2.26	-0.02	2.24	-0.04
PdC <sub>19</sub> PN <sub>3</sub> H <sub>22</sub> S <sub>2</sub> ((Ph) <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> N(Me) <sub>2</sub> -Pd(II)-(SCN)(NCS))	Pd-N	2.15	2.23	0.08	2.09	-0.06
	Pd-P	2.24	2.40	0.16	2.21	-0.03
	Pd-S	2.29	2.68	0.39	2.44	0.15
	Pd-N(NCS)	2.06	2.06	0.00	1.94	-0.12
PdC <sub>6</sub> N <sub>6</sub> H <sub>6</sub> S <sub>3</sub> O (CAXQUN)	Pd-S	2.27	2.44	0.17	2.36	0.09
	Pd-S	2.34	2.52	0.18	2.27	-0.07
	S-Pd-S	95.7	85.3	-10.4	123.7	28.0
	Pd-N	2.04	1.93	-0.11	2.40	0.36
	N-Pd-S	86.5	92.9	6.3	76.1	-10.5
PdC <sub>4</sub> N <sub>4</sub> H <sub>6</sub> S <sub>4</sub> (LESSIL)	Pd-S	2.27	2.51	0.24	2.31	0.04
	S-Pd-S	89.7	83.4	-6.3	86.2	-3.5
PdC <sub>10</sub> N <sub>4</sub> H <sub>20</sub> S <sub>4</sub> (BEWKAP)	Pd-S	2.26	2.53	0.27	2.33	0.07



Table 4 (continued)

	S-Pd-S	90.9	100.3	9.4	96.2	5.3
	Pd-N	2.09	2.05	-0.04	2.05	-0.04
	Pd-N	2.13	2.10	-0.03	2.04	-0.09
PdC <sub>4</sub> N <sub>6</sub> H <sub>8</sub> S <sub>4</sub> (DTHBPD10)	Pd-S	2.30	2.52	0.22	2.32	0.02
	S-Pd-S	92.7	94.8	2.2	93.6	1.0
PdC <sub>14</sub> N <sub>2</sub> H <sub>24</sub> S <sub>4</sub> O <sub>4</sub> (FECTUC)	Pd-S	2.33	2.56	0.23	2.28	-0.05
	S-Pd-S	88.5	71.7	-16.8	86.1	-2.4
PdCl	Pd-Cl	2.42	2.37	-0.05	2.32	-0.10
PdHCl	Pd-Cl	2.35	2.42	0.07	2.28	-0.07
	Pd-H	1.48	1.54	0.06	1.52	0.04
	Cl-Pd-H	85.6	73.5	-12.1	85.3	-0.3
PdCH <sub>3</sub> Cl	Pd-C	1.99	2.23	0.24	2.00	0.01
	Pd-Cl	2.37	2.42	0.05	2.30	-0.07
	C-Pd-Cl	94.5	75.9	-18.6	91.0	-3.5
PdCl <sub>2</sub>	Pd-Cl	2.30	2.36	0.06	2.27	-0.03
	Cl-Pd-Cl	98.4	146.4	48.0	95.6	-2.8
PdC <sub>8</sub> H <sub>12</sub> Cl <sub>2</sub> (CYOCPD02)	Pd-Cl	2.31	2.38	0.07	2.35	0.04
	Cl-Pd-Cl	91.8	70.5	-21.4	97.2	5.4
	Pd-C	2.19	2.33	0.14	2.17	-0.02
PdC <sub>4</sub> N <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> (FEQCOT)	Pd-Cl	2.30	2.43	0.13	2.37	0.07
	Pd-N	1.97	2.03	0.06	1.89	-0.08
	N-Pd-Cl	89.7	76.2	-13.5	90.0	0.3
PdC <sub>4</sub> N <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> (PdCl <sub>2</sub> (MeCN) <sub>2</sub> )	Pd-N	2.03	2.07	0.04	1.97	-0.06
	N-Pd-N	93.9	102.5	8.6	97.8	3.9
	Pd-Cl	2.31	2.41	0.09	2.35	0.04
	N-Pd-Cl	82.0	75.6	-6.4	81.4	-0.7
PdC <sub>4</sub> N <sub>2</sub> H <sub>12</sub> Cl <sub>2</sub> (AMBUPD)	Pd-Cl	2.32	2.40	0.08	2.37	0.05
	Cl-Pd-Cl	95.3	122.0	26.7	110.7	15.3
	Pd-N	2.03	2.21	0.18	2.12	0.09
PdC <sub>4</sub> N <sub>2</sub> H <sub>12</sub> Cl <sub>2</sub> (COGYEC)	Pd-Cl	2.31	2.42	0.11	2.48	0.17
	Pd-N	2.05	2.17	0.12	2.17	0.12
	N-Pd-Cl	87.7	90.8	3.1	78.9	-8.8
PdC <sub>16</sub> N <sub>4</sub> H <sub>24</sub> Cl <sub>2</sub> (BUQRUA)	Pd-Cl	2.31	2.43	0.12	2.39	0.08
	Pd-N	2.02	2.10	0.08	2.00	-0.02
	N-Pd-Cl	94.0	103.0	9.0	90.4	-3.6
PdC <sub>11</sub> N <sub>2</sub> H <sub>10</sub> Cl <sub>2</sub> O (BATTIZ)	Pd-Cl	2.30	2.41	0.11	2.36	0.06
	Cl-Pd-Cl	91.1	69.8	-21.3	101.4	10.3
	Pd-N	2.01	2.14	0.13	2.03	0.02
Pd <sub>2</sub> C <sub>6</sub> H <sub>10</sub> Cl <sub>2</sub> (pi-Allyl palladium chloride dimer)	Pd-Pd	3.52	3.17	-0.35	3.77	0.25
	Pd-Cl	2.48	2.50	0.02	2.48	0.00
	Pd-Pd-Cl	45.1	51.1	6.1	40.7	-4.4
	Pd-C	2.18	2.27	0.09	2.12	-0.06
PdP <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> (cis-Pd(PH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> )	Pd-P	2.32	2.50	0.18	2.33	0.01
	Pd-Cl	2.38	2.42	0.04	2.41	0.03
PdP <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> (trans-Pd(PH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> )	Pd-P	2.35	2.48	0.13	2.34	-0.01
	Pd-Cl	2.37	2.44	0.07	2.42	0.05
PdC <sub>8</sub> H <sub>20</sub> S <sub>2</sub> Cl <sub>2</sub> (trans-Pd(Cl) <sub>2</sub> (SEt <sub>2</sub> ) <sub>2</sub> )	Pd-S	2.44	2.56	0.12	2.30	-0.14
	S-Pd-S	173.4	174.9	1.5	178.0	4.6
	Pd-Cl	2.37	2.43	0.06	2.42	0.05
	S-Pd-Cl	92.6	92.7	0.1	91.0	-1.6
Pd(CO)Cl <sub>3</sub> <sup>-</sup> (KATPEA)	Pd-Cl	2.28	2.41	0.13	2.38	0.10

Table 4 (continued)

	Cl-Pd-Cl	92.8	67.3	-25.6	100.8	8.0
	Pd-C	1.87	2.18	0.31	1.89	0.02
PdCl <sub>4</sub> <sup>2-</sup> (AVUKOR)	Pd-Cl	2.44	2.44	0.00	2.45	0.01
PdC <sub>10</sub> N <sub>2</sub> H <sub>8</sub> C <sub>14</sub> ((C <sub>5</sub> H <sub>4</sub> N) <sub>2</sub> PdCl <sub>4</sub> , BOKHAK)	Pd-Cl	2.29	2.34	0.05	2.31	0.02
	Cl-Pd-Cl	89.1	80.9	-8.2	92.7	3.6
	Pd-N	2.04	2.10	0.06	2.05	0.01
PdCl <sub>6</sub> <sup>2-</sup> (JIZLOT)	Pd-Cl	2.27	2.33	0.06	2.38	0.11
PdTi	Pd-Ti	2.48	2.48	0.00	3.71	1.23
PdV	Pd-V	2.27	2.27	0.00	6.26	3.99
PdCr	Pd-Cr	2.38	2.38	0.00	5.90	3.52
PdMn	Pd-Mn	2.31	2.31	0.00	6.16	3.85
PdFe	Pd-Fe	2.32	2.32	0.00	4.79	2.47
PdCo	Pd-Co	2.42	2.42	0.00	3.56	1.14
PdNi	Pd-Ni	2.43	2.43	0.00	3.77	1.34
PdCu	Pd-Cu	2.38	2.38	0.00	7.69	5.30
PdZn	Pd-Zn	2.41	2.41	0.00	2.79	0.39
PdBr <sub>2</sub>	Pd-Br	2.37	2.49	0.12	2.29	-0.08
	Br-Pd-Br	94.4	100.4	6.0	89.0	-5.4
PdC <sub>10</sub> N <sub>3</sub> H <sub>9</sub> Br <sub>2</sub> (MACGON)	Pd-Br	2.42	2.53	0.11	2.37	-0.05
	Br-Pd-Br	89.1	80.0	-9.1	117.8	28.7
	Pd-N	2.04	2.12	0.08	2.03	-0.01
	N-Pd-Br	91.0	97.2	6.2	71.2	-19.9
PdC <sub>9</sub> N <sub>4</sub> H <sub>12</sub> Br <sub>2</sub> (CH <sub>2</sub> (NC <sub>2</sub> H <sub>2</sub> )(NCH <sub>3</sub> )C) <sub>2</sub> PdBr <sub>2</sub> , AMIPER)	Pd-Br	2.50	2.52	0.02	2.45	-0.05
	Br-Pd-Br	92.6	83.1	-9.5	104.0	11.4
	Pd-N	3.07	3.27	0.20	3.17	0.10
Pd(CO)Br <sub>3</sub> <sup>-</sup> (KATPIE)	Pd-Br	2.41	2.50	0.09	2.44	0.03
	Br-Pd-Br	93.0	88.8	-4.2	97.4	4.3
	Pd-C	1.88	2.12	0.24	1.91	0.03
PdBr <sub>4</sub> <sup>2-</sup>	Pd-Br	2.44	2.54	0.10	2.44	0.00
PdBr <sub>4</sub> <sup>2-</sup> (FETHOB)	Pd-Br	2.43	2.54	0.11	2.55	0.12
PdBr <sub>4</sub>	Pd-Br	2.57	2.55	-0.02	2.56	-0.01
PdZr	Pd-Zr	2.39	2.39	0.00	3.21	0.82
PdMo	Pd-Mo	2.61	2.61	0.00	3.57	0.96
PdAg <sub>2</sub>	Pd-Ag	2.68	2.68	0.00	5.16	2.48
PdF	Pd-F	1.93	2.03	0.10	1.91	-0.02
	Pd-I	2.59	2.57	-0.02	2.48	-0.11
PdI <sub>2</sub>	Pd-I	2.54	2.54	0.00	2.47	-0.07
PdC <sub>16</sub> P <sub>2</sub> H <sub>22</sub> I <sub>2</sub> (IMPPPD01)	Pd-I	2.59	2.53	-0.06	2.60	0.01
	Pd-P	2.33	2.40	0.07	2.24	-0.09
	P-Pd-I	87.6	86.7	-0.9	86.6	-1.0
PdI <sub>4</sub> <sup>2-</sup>	Pd-I	2.76	2.57	-0.19	2.75	-0.01
PdAu <sub>2</sub>	Pd-Au	2.65	2.65	0.00	5.63	2.98
				<b>AM1*</b>		<b>PM6</b>
<i>N=146</i>						
<b>MSE bond length</b>				0.05		0.24
<b>MUE bond length</b>				0.09		0.31
<i>N=46</i>						
<b>MSE bond angle</b>				4.6		1.4
<b>MUE bond angle</b>				14.0		9.2

**Table 5** Calculated AM1\* and PM6 heats of formation and errors compared with our target values for the silver-containing compounds used to parameterize AM1\* (all values are in kcal mol<sup>-1</sup>). Errors that are lower than 10 kcal mol<sup>-1</sup> are shown in regular font, errors of 10–

20 kcal mol<sup>-1</sup> in italics, and errors of greater than 20 kcal mol<sup>-1</sup> in bold. The codenames within parentheses indicate the CSD names [33] of the compounds

Compound	Target $\Delta H_f^\circ$	AM1*		PM6	
		$\Delta H_f^\circ$	Error	$\Delta H_f^\circ$	Error
Ag	68.1	68.1	0.0	68.1	0.0
Ag <sup>-</sup>	37.9	42.8	4.9	-25.4	-63.3
Ag <sup>+</sup>	242.7	241.2	-1.5	233.5	-9.2
Ag <sub>2</sub>	98.0	99.8	1.8	100.3	2.3
Ag <sub>2</sub> <sup>-</sup>	72.6	46.5	-26.1	6.4	-66.2
AgH	67.0	62.1	-4.9	77.6	10.6
AgH <sup>+</sup>	289.1	293.1	4.0	280.6	-8.5
AgH <sub>2</sub>	113.2	121.9	8.6	129.4	16.2
AgCH <sub>3</sub>	93.5	60.0	-33.5	57.3	-36.2
AgCH <sub>3</sub> <sup>+</sup>	283.2	260.2	-23.1	247.5	-35.7
AgNH <sub>2</sub>	97.3	67.1	-30.2	68.4	-28.9
Ag(NH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	109.1	91.3	-17.8	113.1	4.0
Ag(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	321.0	331.6	10.6	317.4	-3.6
Ag(CN) <sub>2</sub> <sup>-</sup>	50.4	47.1	-3.3	56.8	6.4
AgO	53.0	56.9	3.9	98.2	45.2
AgOH	25.9	12.1	-13.8	31.2	5.3
Ag(H <sub>2</sub> O) <sub>6</sub> <sup>+</sup>	-217.8	-214.6	3.2	-170.4	47.4
AgF	2.0	45.3	43.3	-1.8	-3.8
AgOF	68.3	54.1	-14.2	80.4	12.1
AgF <sub>3</sub>	-2.7	-2.8	-0.1	-86.2	-83.5
AgAlH <sub>2</sub>	93.1	91.6	-1.5	92.7	-0.4
AgAl	106.1	112.7	6.6	75.5	-30.6
AgSiH <sub>3</sub>	81.6	81.6	0.0	109.4	27.8
AgPH <sub>2</sub>	76.0	76.0	0.0	-46.5	-122.5
AgS	91.2	74.0	-17.2	66.1	-25.1
AgSH	40.8	41.7	0.9	40.2	-0.6
AgCl	22.0	66.2	44.2	22.1	0.1
AgCH <sub>2</sub> Cl <sup>-</sup>	5.6	5.5	-0.1	-47.2	-52.8
AgOCl	43.9	8.4	-35.5	110.2	66.3
AgOBr	72.9	42.5	-30.4	137.4	64.5
AgBr	25.0	56.8	31.8	32.4	7.4
AgBr <sub>2</sub>	55.1	55.1	-0.1	59.2	4.1
AgI	41.6	74.4	32.8	56.9	15.3
AgTi	84.9	84.9	-0.1	93.2	8.3
AgV	106.3	163.9	57.6	184.8	78.5
Ag <sub>2</sub> Mn	299.8	299.8	0.0	202.3	-97.5
Ag <sub>2</sub> Fe	185.0	185.0	0.0	210.9	25.9
AgCr	189.1	189.1	0.0	178.7	-10.4
AgCo	163.3	163.2	-0.1	123.9	-39.4
AgNi	102.1	120.0	17.9	155.3	53.2
AgCu	110.4	97.8	-12.6	170.6	60.2
AgZn	92.0	92.0	0.0	-67.7	-159.7
AgZr	186.9	101.5	-85.4	155.3	-31.6
AgMo	243.8	243.7	-0.1	219.9	-23.9
AgAu	114.3	114.3	0.0	154.4	40.1

**Table 5** (continued)

	AM1*	PM6
<i>N</i> =45		
<b>Most positive error</b>	57.6	78.5
<b>Most negative error</b>	-85.4	-159.7
<b>MSE</b>	-1.8	-7.4
<b>MUE</b>	13.9	34.1
<b>RMSD</b>	23.0	48.6
<b>Results for the PM6 parameterization set (<i>N</i>=13)</b>		
<b>MSE</b>	5.9	2.4
<b>MUE</b>	14.5	5.0
<b>RMSD</b>	20.9	6.3

include these model compounds, which seriously affects the statistics. For the bond angles, PM6, with an MUE of 9.2°, performs better than AM1\* (MUE=14.0°). Both AM1\* and PM6 overestimate bond angles to palladium-containing compounds by 4.6° and 1.4°, respectively.

## Silver

### Heats of formation

The results obtained for the heats of formation of silver-containing compounds are shown in Table 5. Once again, we have compared our results with PM6.

AM1\*, with an MUE of 13.9 kcal mol<sup>-1</sup>, reproduces the heats of formation of the training set of palladium compounds used in the parameterization better than PM6 (MUE=34.1 kcal mol<sup>-1</sup>). Here one must consider that this comparison is not strictly valid, as it is based on the current parameterization data, which differ from those used in PM6 parameterization. The AM1\* parameterization data set contains 45 compounds, of which 13 are taken from the original PM6 parameterization data set. These data demonstrate the influence of the extent of the training data. PM6 performs better (MUE=5.0 kcal mol<sup>-1</sup>) than AM1\* (MUE of 14.5 kcal mol<sup>-1</sup>) for the subset for which it was trained.

Both AM1\* and PM6 underestimate the heats of formation of silver compounds by only -1.8 and -7.4 kcal mol<sup>-1</sup> (MSE), respectively. The largest positive errors for AM1\* are found for the compounds AgV (57.6 kcal mol<sup>-1</sup>), AgCl (44.2 kcal mol<sup>-1</sup>) and AgF (43.3 kcal mol<sup>-1</sup>). The largest negative errors for AM1\* are found for AgZr (-85.4 kcal mol<sup>-1</sup>), AgOCl (-35.5 kcal mol<sup>-1</sup>) and AgCH<sub>3</sub> (-33.5 kcal mol<sup>-1</sup>).

### Ionization potentials and dipole moments

A comparison of the calculated and experimental ionization potentials and dipole moments of silver-containing compounds for AM1\* and PM6 are shown in Table 6.

AM1\* overestimates Koopmans' theorem ionization potentials of silver-containing compounds, with an MSE of 0.48 eV, whereas PM6 underestimates them by -0.36 eV. AM1\* performs better than PM6 (MUE=1.16 eV), with an MUE of 0.98 eV for ionization potentials of silver compounds. Large errors—more than 1 eV—for AM1\* are found for Ag<sub>2</sub>, AgCu and AgF (2.35, 1.63 and -1.52 eV, respectively).

Both AM1\* and PM6 tend to give positive systematic errors for dipole moments of silver-containing compounds, with MSEs of 0.96 and 1.51 debyes, respectively. AM1\*, with an MUE of 1.75 debyes, performs better than PM6 (2.00 debyes) for dipole moments of silver-containing compounds. For AgOCl and AgOBr, both AM1\* and PM6 give extremely large (more than 4 debyes) errors. Reference values for these two compounds were taken from the PM6 parameterization dataset and calculated at the B88-PW91/DZVP level by Stewart [36].

### Geometries

The geometrical variables used to parameterize AM1\* for silver and a comparison of the AM1\* and PM6 results are shown in Table 7.

AM1\* shows no systematic error trend (MSE=0.01 Å) for bond lengths in silver compounds, whereas PM6 overestimates them by 0.27 Å. AM1\*, with a mean unsigned error of 0.10 Å, performs far better than PM6

**Table 6** Calculated AM1\* and PM6 Koopmans' theorem ionization potentials and dipole moments for silver-containing compounds. The errors are coded as follows: up to 0.5 eV or 0.5 debyes is shown in

regular font, between 0.5 and 1.0 is shown in italics, and larger than 1.0 is shown in bold

Compound	Target	AM1*		PM6	
			Error		Error
<b>Koopmans' Theorem Ionization Potentials for Silver Compounds (eV)</b>					
Ag <sub>2</sub>	7.66	10.00	2.35	9.95	2.29
AgH	9.23	10.13	0.90	9.10	-0.13
AgF	11.00	9.48	-1.52	8.17	-2.83
AgAl	7.80	7.61	-0.19	8.69	0.89
AgCl	10.08	9.78	-0.30	8.53	-1.55
AgCu	7.78	9.41	1.63	7.10	-0.68
AgBr	9.59	9.82	0.23	8.75	-0.84
AgI	8.80	9.55	0.75	8.77	-0.03
		<b>AM1*</b>		<b>PM6</b>	
<i>N=8</i>					
<b>MSE</b>		0.48		-0.36	
<b>MUE</b>		0.98		1.16	
<b>Dipole Moments for Silver Compounds (Debye)</b>					
AgCN	7.36	6.11	-1.25	7.00	-0.36
AgF	5.91	5.28	-0.63	6.89	0.98
AgOF	0.16	0.10	-0.06	1.19	1.03
AgCl	6.12	5.28	-0.84	6.55	0.43
AgOCl	0.68	5.75	5.07	6.52	5.84
AgBr	5.82	5.91	0.09	4.45	-1.37
AgOBr	1.81	6.13	4.32	5.82	4.01
		<b>AM1*</b>		<b>PM6</b>	
<i>N=7</i>					
<b>MSE</b>		0.96		1.51	
<b>MUE</b>		1.75		2.00	

(MUE=0.44 Å) for bond lengths. Here, once again, we note that the large PM6 errors for bond lengths resulted from silver–transition metal diatomic model compounds, and that these compounds are not covered by the PM6 parameterization dataset.

Both AM1\* and PM6 give negative systematic errors for bond angles of silver-containing compounds. While AM1\* underestimates them by only  $-0.4^\circ$ , PM6 underestimates by a much larger value ( $-4.7^\circ$ ). The MUEs for AM1\* and PM6 are found to be  $14.9^\circ$  and  $21.7^\circ$ , respectively. Although AM1\* performs better than PM6 for bond lengths, these mean unsigned errors are still considered to be high.

## Discussion

In this work, we have presented our new AM1\* parameters for palladium and silver. These provide important additional elements for the chemistry of organometallic and biological catalysts and for biochemical systems. We have aimed to produce a parameter set that is more robust and generally applicable than the ones trained only using experimental data. We have extended the range of the parameterization dataset, and made it more reliable by checking experimental data and including results from DFT calculations. AM1\* parameterizations for palladium and

**Table 7** Calculated AM1\* and PM6 bond lengths and angles for silver-containing compounds. The codenames within parentheses indicate the CSD names [33] of the compounds. The errors are coded

as follows: errors of up to 0.05 Å or 0.5° is shown in regular font, errors of 0.05–0.1 Å or 0.5–1.0° are shown in italics, and errors larger than 0.1 Å or 1° are shown in bold

Compound	Variable	Target	AM1*		PM6	
				Error		Error
AgH <sup>+</sup>	Ag-H	1.82	1.63	-0.19	1.59	-0.23
AgH	Ag-H	1.62	1.62	0.00	1.63	0.01
AgCN	Ag-C	2.11	2.12	0.01	2.01	-0.10
	C-N	1.18	1.16	-0.02	1.15	-0.03
AgC <sub>2</sub> N <sub>2</sub> <sup>-</sup>	Ag-C	2.13	2.14	0.01	2.09	-0.04
	C-N	1.13	1.17	0.04	1.16	0.03
AgC <sub>3</sub> N <sub>3</sub> H <sub>8</sub> (FILSEZ)	Ag-N	2.28	2.24	-0.04	2.46	0.18
	Ag-N'	2.36	2.67	0.31	2.49	0.13
	Ag-C	2.06	2.11	0.05	2.07	0.01
	N-Ag-N'	76.6	73.6	-3.0	73.0	-3.6
Ag(NH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	Ag-N	2.50	2.36	-0.14	2.30	-0.20
AgO	Ag-O	2.00	2.12	0.12	2.03	0.03
AgOH	Ag-O	2.09	2.15	0.06	2.02	-0.07
	O-H	0.98	0.96	-0.02	0.92	-0.06
	Ag-O-H	106.8	106.9	0.1	119.1	12.3
Ag(NCO) <sub>2</sub> <sup>-</sup>	Ag-N	2.13	2.13	0.00	2.08	-0.05
AgF	Ag-F	2.05	2.04	-0.01	1.98	-0.07
Ag(O)F	Ag=O	1.94	2.04	0.10	1.41	-0.53
	Ag-F	1.99	2.03	0.04	2.03	0.04
AgC <sub>5</sub> NH <sub>3</sub> F <sub>7</sub> <sup>-</sup> (DUJXEL)	Ag-N	2.08	2.03	-0.05	2.23	0.15
	Ag-C	2.10	2.12	0.02	2.22	0.12
AgAl	Ag-Al	2.47	2.47	0.00	2.47	0.00
Ag(PH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Ag-P	1.81	2.28	0.47	1.96	0.15
AgS	Ag-S	2.42	2.28	-0.14	2.41	-0.01
AgHS	Ag-S	2.41	2.29	-0.12	2.36	-0.05
	S-H	1.36	1.43	0.07	1.35	-0.01
	Ag-S-H	94.8	94.6	-0.2	97.9	3.1
AgC <sub>2</sub> N <sub>8</sub> H <sub>12</sub> S <sub>2</sub> <sup>+</sup> (TCBZAG)	Ag-N	2.51	2.83	0.32	3.85	1.34
	Ag-S	2.44	2.35	-0.09	2.46	0.02
	Ag-N	2.51	2.83	0.32	3.84	1.33
	S-Ag-N	77.2	76.5	-0.7	50.2	-27.0
	N-Ag-N	98.7	118.9	20.2	77.8	-20.9
	N-Ag-N-S	-123.1	-100.1	23.0	-86.5	36.6
AgC <sub>12</sub> N <sub>6</sub> H <sub>18</sub> S <sub>3</sub> <sup>+</sup> (ZUVVIV)	Ag-S	2.51	2.27	-0.25	2.55	0.04
	S-C	1.69	1.76	0.07	1.68	-0.01
	C-S-Ag	106.3	116.4	10.1	136.3	30.1
	S-Ag-S	115.7	148.5	32.8	97.7	-18.0
AgCl	Ag-Cl	2.38	2.25	-0.13	2.32	-0.06
AgCH <sub>3</sub> Cl	Ag-C	2.17	2.15	-0.02	2.13	-0.04
	Ag-Cl	2.48	2.48	0.00	2.44	-0.04
AgClO	Ag=O	1.97	2.12	0.15	1.41	-0.56
	Ag-Cl	2.33	2.36	0.03	2.43	0.10
AgC <sub>6</sub> N <sub>2</sub> H <sub>14</sub> SCl (VUHCAC)	Ag-N	2.41	2.84	0.43	2.71	0.30
	Ag-Cl	2.40	2.38	-0.02	2.38	-0.02
	Ag-S	2.63	2.22	-0.41	2.52	-0.11
	N-Ag-N	73.6	58.0	-15.6	59.6	-14.0
	Cl-Ag-N	136.2	105.8	-30.4	91.2	-44.9
AgC <sub>8</sub> H <sub>16</sub> S <sub>2</sub> ClO <sub>6</sub> (CIJBIG)	Ag-S	2.41	2.16	-0.25	2.45	0.04
	Ag-O	2.62	2.12	-0.50	3.88	1.26

Table 7 (continued)

	S-Ag-S	160.3	118.1	-42.2	180.0	19.7
	O-Ag-S	102.7	103.3	0.6	72.5	-30.1
AgBr	Ag-Br	2.48	2.58	0.10	2.18	-0.30
AgBrO	Ag=O	1.92	2.16	0.24	1.39	-0.53
	Ag-Br	2.44	2.53	0.09	2.50	0.06
Ag <sub>2</sub>	Ag-Ag	2.66	2.66	0.00	2.65	-0.01
Ag <sub>2</sub> <sup>-</sup>	Ag-Ag	2.77	2.72	-0.05	3.04	0.27
AgH <sub>2</sub>	Ag-H	1.76	1.89	0.12	1.81	0.04
AgCH <sub>3</sub>	Ag-C	2.12	2.16	0.03	2.08	-0.05
AgCH <sub>3</sub> <sup>+</sup>	Ag-C	2.33	2.56	0.24	2.01	-0.32
Ag(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	Ag-N	2.85	2.85	0.00	2.47	-0.38
	Ag-N'	2.29	2.30	0.01	2.42	0.13
AgC <sub>6</sub> H <sub>5</sub>	Ag-C	2.10	2.15	0.05	2.05	-0.05
Ag(CH <sub>3</sub> ) <sub>2</sub>	Ag-C	2.16	2.20	0.05	2.26	0.10
AgNH <sub>2</sub>	Ag-N	2.08	2.15	0.07	2.05	-0.03
Ag(H <sub>2</sub> O) <sub>6</sub> <sup>+</sup>	Ag-O	2.53	2.52	-0.01	3.67	1.14
AgF <sub>2</sub>	Ag-F	1.96	2.03	0.07	2.00	0.04
AgAlH <sub>2</sub>	Ag-Al	2.48	2.48	0.00	2.37	-0.11
AgSiH <sub>3</sub>	Ag-Si	2.42	2.51	0.09	3.37	0.95
AgPH <sub>2</sub>	Ag-P	2.43	2.43	0.00	1.49	-0.94
AgCl <sub>2</sub>	Ag-Cl	2.34	2.23	-0.11	2.36	0.02
AgBr <sub>2</sub>	Ag-Br	2.50	2.46	-0.04	2.26	-0.24
AgI	Ag-I	2.62	2.40	-0.22	2.01	-0.61
AgTi	Ag-Ti	2.69	2.69	0.00	3.48	0.79
AgV	Ag-V	2.65	2.65	0.00	4.13	1.48
Ag <sub>2</sub> Mn	Ag-Mn	2.70	2.70	0.00	4.96	2.26
Ag <sub>2</sub> Fe	Ag-Fe	2.56	2.52	-0.04	4.41	1.85
AgCr	Ag-Cr	2.57	2.57	0.00	5.41	2.84
AgCo	Ag-Co	2.65	2.65	0.00	3.68	1.03
AgNi	Ag-Ni	2.64	2.49	-0.15	4.78	2.14
AgCu	Ag-Cu	2.42	2.49	0.07	4.37	1.94
AgZn	Ag-Zn	2.66	2.77	0.11	2.54	-0.12
AgZr	Ag-Zr	2.79	2.90	0.12	3.23	0.45
AgMo	Ag-Mo	2.71	2.72	0.01	3.83	1.12
AgAu	Ag-Au	2.59	2.59	0.00	4.13	1.54
				<b>AM1*</b>		<b>PM6</b>
<i>N</i> =72						
<b>MSE bond length</b>				0.01		0.27
<b>MUE bond length</b>				0.10		0.44
<i>N</i> =12						
<b>MSE bond angle</b>				-0.4		-4.7
<b>MUE bond angle</b>				14.9		21.7

silver give very good energetic and electronic results and also perform very well for the structural properties for our extended training set. Both AM1\* and PM6 extend the range of applicability of NDDO-based MNDO-like techniques and provide good starting points for possible forth-

coming reaction-specific local parameterizations and comparison calculations.

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